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PROTECTIVE COATINGS FOR METALS

BY

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GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, secretary of the society, Washington, D. C.; the late John E. Teeple, then treasurer of the society, New York; and Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the A. C. S. series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successors) of New York.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed editors (the present list of whom appears at the close of this introduction) to have charge of securing authors, and of considering critically the manuscripts submitted. The editors endeavor to select topics of current interest, and authors recognized as authorities in their respective fields.

The development of knowledge in all branches of science, especially in chemistry, has been so rapid during the last fifty years, and the fields covered by this development so varied that it is difficult for any individual to keep in touch with progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and by such compendia as Beilstein's Handbuch der Organischen Chemie, Richter's Lexikon, Ostwald's Lehrbuch der Allgemeinen Chemie, Abegg's and Gmelin-Kraut's Handbuch der Anorganischen Chemie, Moissan's Traité de Chimie Minérale Générale, Friend's and Mellor's Textbooks of Inorganic Chemistry and Heilbron's Dictionary of Organic Compounds, it often takes a great deal of time to coördinate the knowledge on a given topic. Consequently when men who have spent years in the study of important subjects are willing to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value. It was with a clear recognition of the usefulness of such work that the American Chemical Society undertook to sponsor the publication of the two series of monographs.

Two distinct purposes are served by these monographs: the first, whose fulfillment probably renders to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a form intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs enable such men to form closer contact with work in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well-digested survey of the progress already made, and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, extended references to the literature enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection is made of those papers which are most important.

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Preface

In 1927 H. S. Rawdon's *Protective Metallic Coatings* appeared in the present monograph series. When, about three years ago, it became time to revise the work, Mr. Rawdon felt himself unable to undertake the task. The present authors were then invited, with Mr. Rawdon's kind consent, to prepare the revision. After a survey of the field it was concluded that the scope should be enlarged to include protective coatings of all types, including paints. It was felt that in this way the reader interested in corrosion prevention might be given more comprehensive information on the subject.

It was expected originally that the present treatise would consist essentially in a revision of Mr. Rawdon's earlier work enlarged in scope. Owing to the great technological advances of the past decade and the thousands of papers which have appeared in the protective coating field it soon became evident that a new treatise was desirable.

The present volume is designed primarily for those who have problems of protection; it is not intended to be a manual for the production of protective coatings although considerable information is given on this phase of the subject so that the reader may have a better understanding of the nature of the various coatings. As far as practicable, patented coatings and methods are so indicated in the references; but the absence of patent reference does not necessarily imply that a means or method is in the public domain. Neither should it be assumed that the mention of any patented or proprietary coating is in any sense a recommendation for the application or use of such coating.

Chapters 13, 14 and 15 were written by Mr. Schuh, who was at the time a member of the technical staff of Bell Telephone Laboratories. The other chapters have been prepared by the senior author. In a number of chapters and particularly in Chapter 4, having to do with hot-dipped coatings, it has been possible to utilize considerable material from Mr. Rawdon's monograph; also a number of the illustrations in that work have been reproduced.

The authors are greatly indebted for critically reading portions of the manuscript and for helpful advice to: C. W. Borgmann, formerly of the National Tube Co. but now of the University of Colorado, W. H. Finkeldey of Singmaster and Breyer, G. O. Hiers of the National Lead Co., W. W. Higgins of the A. O. Smith Co., R. J. McKay and W. A. Wesley of the International Nickel Co., D. J. Macnaughton, T. P. Hoar, and W. E. Hoare of International Tin Research and Development Council, London, R. B. Mears of the Aluminum Company of America, E. E. Poste of Chattanooga, Tenn., L. R. Schlundt of Republic Lead Equipment Co., W. Blum, I. A. Denison, K. H. Logan, S. P. Ewing and E. F. Hickson of the National

Bureau of Standards, M. Brown of the Western Electric Co., and H. G. Arlt, W. E. Campbell, K. G. Compton, C. D. Hocker and C. H. Sample, their colleagues in Bell Laboratories.

Particular thanks are due to H. E. Haring, who critically read the entire manuscript and collaborated in the preparation of Chapter 1.

Finally, the authors take pleasure in expressing their appreciation to R. R. Williams, Chemical Director of the Bell Telephone Laboratories, for his encouragement and advice.

New York, N. Y. R. M. BURNS
November 15, 1938

Foreword

The advances which have been made in the metal-coating industry during the past decade have been so numerous and important that one is inclined to speak in superlatives in referring to them. In the class of metallic coatings, these advances have been especially striking in the field of electroplating. Not only have plating methods been extended and applied on a mass production scale, as in the zinc coating of wire and the tin plating of continuous steel strip, but entirely new processes, such as "bright plating," have been developed. The commercial application of these with the attendant saving in labor has been of great importance. The perfecting of the anodic oxidation process for aluminum has assisted greatly in successfully establishing the position of this metal as an engineering structural material and much the same can be said of magnesium. Improvements in older methods of coating, though not so spectacular, have been just as important industrially, as is evidenced by the exceedingly widespread use of the phosphate treatment for sheet steel in automobile bodies and other shapes prior to the application of the finishing coat. The success attained in the development of new and improved finishes of an organic nature is familiar to every user of metal products.

The body of information on protective coatings for metals resulting from the investigations on this subject in the years which have elapsed since the appearance of the previous monograph on the subject is so great that when the subject of revision arose, the preparation of an entirely new book appeared to be the most desirable course to follow. The need for information on coatings of a nonmetallic nature which are now so widely used in competition with or interchangeably with metallic coatings prompted the extension of the scope of the monograph to include paints and other applied organic coatings.

The active interest manifested during the past few years in investigations on the general subject of the corrosion of metals has led to the carrying-out of long-time exposure tests which yielded much new basic information having a direct bearing on our knowledge of the useful life of coatings and coated metals. The authors have wisely incorporated a great deal of this information in the discussion of the different types of coatings. Likewise, it has been deemed desirable to devote considerable space to the preliminary preparation of metal surfaces before the application of the coating since the quality of any coating is so dependent upon this factor.

The new monograph, therefore, covers a much broader field than did the previous one which was really a pioneer in the field of metallic coatings.

The investigator of the abstruse problems of corrosion as well as the materials engineer seeking practical help in combating this problem by preventing corrosion by protecting the surface will find this volume a veritable mine of information on all phases of the subject.

December 8, 1938 H. S. RAWDON
National Bureau of Standards
Washington, D. C.

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Chapter 1

Protective Coatings and the Mechanism of Corrosion

Many metals of industrial importance, notably iron and steel, require protection against corrosion. The character and extent of the necessary protective measures depend upon the nature of the metal, and of the environment to which the metal is exposed. There are a number of general methods for the preservation of metals. Where control of the environment is feasible, it may be possible to eliminate or minimize one or more of such corrosive factors as oxygen, humidity, dust and sulfurous gases. Among common examples of this method are deaeration of water in boilers and closed water systems,[1] and reduction of atmospheric pollution by means of air-conditioning apparatus. Measures of this kind are exceedingly effective in extending the useful life of metals and metallic products. All other methods of corrosion control seek to interpose a protective film between the metal and its surroundings, and it is with this subject that the present monograph is concerned.

Protective coatings may be formed naturally or synthetically, or by both methods. In reality, naturally formed protective coatings are corrosion products of a certain character which may be obtained by the introduction of the protective agent into the metal, as, for example, the use of chromium and nickel in alloy steels, or tin in Admiralty metal; or the films may be produced by purposely adding the protective constituent to the environment, as in the use of soluble chromates in recirculating water systems, automobile radiators, and air-conditioning equipment. The relatively good corrosion resistance of the common non-ferrous metals is due to the nature of the surface films which these metals develop in ordinary environments. In any case, these self-formed protective films are the result of the conversion of the metal surface into a chemical compound which is held to the surface by atomic forces. Such films are usually continuous, of low solubility, relatively impermeable, and often invisible. Noble metals may form protective films under some circumstances, but in general the relative incorrodibility of these metals as a class is due to their chemically unreactive character.

Synthetic protective coatings are of great variety. The two most common classes are metallic coatings, employing almost any non-ferrous metal except the alkali and alkaline earth metals, and organic coatings which may consist of paints, lacquers, enamels, oils, waxes or bitumins. Coatings of inorganic substances such as vitreous enamels, cement, concrete and clay products, while relatively less important, are coming into wider use for certain purposes. These three types of coating have their advantages and their limitations. The following chapters will describe in some detail what these coatings are, how they are obtained and evaluated, and how they perform. Before undertaking this project, however, it would seem appropriate to consider at some length the nature of corrosion processes and how these are affected by the presence of protective coatings.

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[1] Speller, F. N., "Corrosion, Causes and Prevention," 2nd ed., p. 384, New York, McGraw-Hill Book Co., 1935.

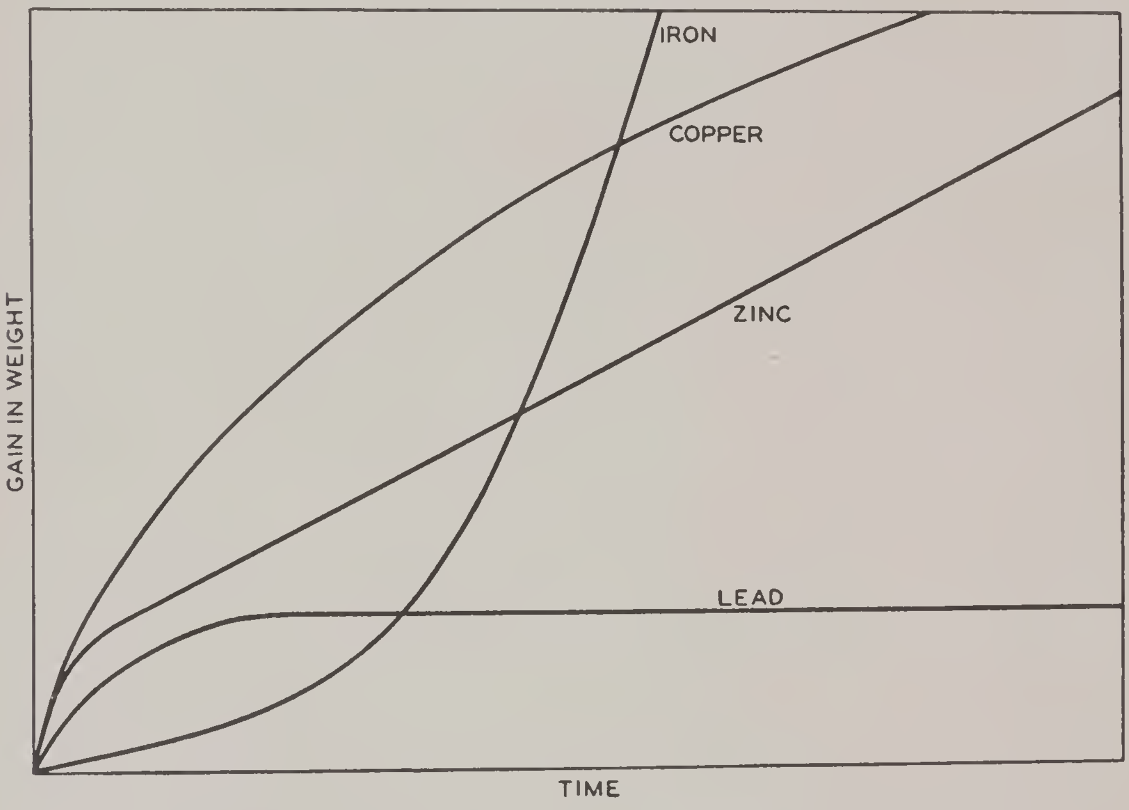

Figure 1.—Corrosion-Time Relationships of Certain Metals Exposed to the Atmosphere.

The metallic state is uncommon in nature. It is well recognized, as implied above, that metals corrode by means of chemical reactions with the non-metallic elements of their surroundings. The more heterogeneous the metal and the more complex the environment, the more complicated may be the process of corrosion. The composition, physical state and surface condition of the metallic material, as well as the chemical components of the surrounding medium—their phases and concentrations—determine the nature of corrosion reactions. Other important variables affecting corrosion processes are the temperature, temperature fluctuation, movement or circulation of the medium in contact with the metal surface, the nature and solubility of the corrosion products, and particularly the position in which these products are precipitated with reference to the surface of the corroding metal. In spite of all these complexities it is generally possible, from an understanding of the mechanism of corrosion and from observations of corrosion behavior, to recognize the controlling variables in given instances of corrosion.

In this connection it is of interest to consider the film-forming characteristics of certain metals exposed to indoor summer atmosphere. Figure 1 gives the gain in weight with time for copper, zinc, lead and iron for such exposure.[2] Rain, relative humidity, atmospheric pollution, dust, and temperature and temperature fluctuation may all have a bearing upon the results obtained for individual metals in ordinary atmospheres. It will be observed that the relationship for copper is parabolic in type, indicating that the process is controlled by the rate of diffusion of oxygen or other reactants through an increasingly thicker surface film, presumably of oxide. Silver is known to display a similar characteristic, even at very high humidities, and the film consists of silver sulfide. Thin films formed on copper in pure air are impervious to volatile sulfur compounds but oxide films produced on silver appear to be converted to sulfide by subsequent exposure to air containing sulfurous gases. The curve shown for zinc, which may be obtained for iron also under certain circumstances,[3] is in harmony with the view [3a] that the oxide first formed is pseudomorphic with the underlying metal, and that upon attaining a certain thickness the film becomes granular in character and does not further influence the rate of corrosion. The corrosion-time curve for lead becomes parallel with the time axis after the initial stages. The film in this case becomes impervious to the constituents of the environment and is the so-called "self-healing" type, of which the air-formed film on aluminum is another example.

The curve shown for iron in Figure 1, which may be obtained also for nickel, copper, zinc and many other metals at high humidities, indicates that the film which forms in the initial stages of the exposure exerts an accelerating influence upon the subsequent rate of corrosion. Iron displays a markedly lower "critical" humidity which falls within the range 40 to 65 per cent relative humidity, and this humidity range probably obtained in the case under consideration. By the term critical humidity is meant the relative humidity corresponding to the vapor pressure of a saturated solution of the corrosion products, and this depends upon the composition and to some extent the structure of these products. In other words the acceleration of corrosion is due in such cases to the water taken up by the corrosion products. The nature of the films which form on iron in the atmosphere at ordinary and elevated temperatures has lately been studied extensively by a number of investigators.[4] Curves of almost all the

[2] Adapted from Vernon, W. H. J., *Trans. Faraday Soc.*, 19, 839 (1924); 23, 113 (1927).

[3] Vernon, W. H. J., *Trans. Faraday Soc.*, 31, 1668 (1935).

[3a] Finch, G. I., and Quarrell, A. G., *Proc. Phy. Soc.*, 46, 148 (1934).

[4] See reference 3 and also Miley, H. A., and Evans, U. R., *J. Chem. Soc. (London)*, 1295 (1937); Miley, H. A., *Metallurgist*, Supplement to *Engineer*, 11, April 30, June 25 (1937).

characteristics illustrated in Figure 1 may be had under the appropriate circumstances. It would appear that there are at least two forms of ferric oxide, one of which (α-Fe_2O_3) is stable above 200° C. and protective in character, and the other (γ-Fe_2O_3) stable below that temperature and more open and non-protective in structure. Very likely the films formed under ordinary atmospheric conditions are more or less hydrated.

Corrosion is a degradation process and is therefore characterized by the dissipation of energy in some form. The best measure of the tendency of a metal to corrode is, in thermodynamical terms, the decrease in free energy accompanying the reaction, *i.e.*, the difference in energy between the initial and final states of the system. This may be obtained by simple calculation and is of value in showing whether or not it is possible for corrosion to occur under the conditions defined.[5] There is no assurance, however, that reactions which are possible will actually take place within a reasonable time, if indeed at all. Once it is determined by calculation that a metal may corrode in a given environment, the problem becomes one of determining the rate of the reaction. Since this rate bears no direct relationship to the energy changes which are involved it cannot be predicted, but must be measured in some fashion.[6]

There are two general classes of corrosion reactions: those in which there is a direct combination of metal and non-metallic elements, and those in which the metal replaces hydrogen (or another metal) in compounds. The former is exemplified by oxidation, halogenation or sulfurization reactions, usually more evident at somewhat elevated temperatures or low humidities. The kinetics of individual reactions may be complex and often obscure. The second class of reactions usually involves replacement, by the corroding metal, of hydrogen from water or acids; this is well known to be an electrolytic process. Recent theoretical studies have indicated that reactions of the first class may be also electrolytic in character.[6a] When metals corrode in the atmosphere either or both of these mechanisms may be involved depending upon circumstances. However, the practical problem of corrosion is chiefly concerned with replacement type reactions which occur in the presence of moisture. In view of this fact it seems desirable to examine the mechanism of this type of corrosion reaction in some detail.

It has been well established that, in the corrosion of a metal in aqueous environment, two reactions take place simultaneously upon its surface; metal ions pass into solution and hydrogen ions pass out of solution to form hydrogen gas, or combine with atmospheric oxygen to form water.* However, inasmuch as ions are matter and have dimensions, it is evident that both reactions cannot take place at the same point and that there must be two kinds of areas, those at which metal dissolves, and those at which hydrogen ions are discharged or consumed by oxygen. In postulating such a situation it is necessary to assume that the interface between a metal and its environment is not entirely homogeneous; otherwise there would be no basis for the selection and establishment of those two kinds of areas. There are in other words two types of interface between metal and environment at which different corrosion tendencies must exist. The known resistance of spectroscopically pure metals to solution even in acid is the result of the homogeneity of the metal-acid interface and not of a lesser tendency of the metals to dissolve. Unless specially prepared, metal surfaces contain areas which are chemically or physically different from the rest of the surface. The presence of metallic impurities, oxides, and differences in crystal structure and physical strain, which in turn lead to differences in solution tendencies, cannot readily be avoided. In actual practice, therefore, it is safe to assume that perfectly homogeneous metals are not commercially available; and even if they were, the chances of their environments being equally homogeneous are rather remote.

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[5] Forrest, H. O., Roetheli, B. E., and Brown, R. H., *Ind. Eng. Chem.*, 23, 650 (1931).

[6] Johnston, J., *Ind. Eng. Chem.*, 26, 1238 (1934).

[6a] Wagner, C., *Z. Phys. Chem.*, *B*, 21, 25 (1933); Hoar, T. P. and Price, L. E., *Trans. Faraday Soc.*, 34, 867 (1938).

* In neutral solution it is likely that the last-mentioned reaction consists merely in the formation of oxygen (or hydroxyl ions).

These areas of different solution tendency can be shown experimentally to have different electrolytic potentials. In the "galvanic cells" so formed, the areas which favor metal dissolution are the anodes, and those which favor hydrogen-ion discharge (or hydroxyl-ion formation from oxygen) are the cathodes.* The quantity of current which passes through these cells is proportional to the amount of metal which dissolves. This "couple" action provides the mechanism by means of which corrosion takes place.

The basis of any electrochemical treatment of the subject of corrosion is, of necessity, the "electromotive force series," an arrangement of the elements in the order of their dissolution tendencies. The position of some of the more common metals (and non-metals) in this series is shown below. The values of potential given are those calculated for the elements in solutions containing *in effect* one atomic weight in grams of ions in 1000 grams of water at 25° C.† For gas electrodes the gas pressure is assumed to be one atmosphere.

These standard potentials may be considered as the voltage of electrolytic cells in which one pole is the hydrogen electrode, designated arbitrarily as zero, and the other is the electrode in question. The sign of the electrode indicates its polarity in such a cell.

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* Expressed in terms of electron transfer, the anodes are areas which tend to gain (or accept) electrons by the formation of positively charged ions (cations) or the discharge of negatively charged ions (anions); conversely the cathodes are areas which tend to lose electrons by the discharge of cations or the formation of anions.

† Actually more than one atomic weight in grams of a metal is required to obtain the theoretical ionic activity of one gram atomic weight in 1000 grams of water. For this reason the term "in effect" is employed and will later be implied when mention is made of ionic concentration. Solutions involved in most corrosion problems are so dilute that the actual and effective concentrations are of similar magnitude.

The fact cannot be too strongly emphasized that the relative position of any one of the metals (or non-metals) in the series is dependent not only upon its inherent solution or corrosion tendency, but also upon the effective concentration of ions of that metal which exists in the environment. It is well known that for every tenfold increase in the ionic concentration of a metal in its environment, the tendency for that metal to dissolve or corrode is decreased, that is, it becomes more electropositive by $\frac{0.059}{n}$ volt at 25° C., where n is the number of unit electrical charges on the ion, or in other words, the valence of the metal. The potential of non-metals varies with concentration in like manner, with the difference that in this case an increase in ionic concentration causes the electrode to become more electronegative. The significance of the concentration factor in determining the position of a metal in the e.m.f. series is well illustrated by the fact that the positions of two metals so far apart as zinc and copper can be reversed, *e.g.*, in zinc cyanide solution. Under such circumstances copper dissolves or corrodes more readily than zinc and actually displaces zinc from solution.

Another fact which must be taken into consideration in utilizing the e.m.f. series is that the gas electrodes, such as the hydrogen and oxygen electrodes included therein are assumed to be *at atmospheric pressure.* The concentration of gas in an electrode is equally as important in the establishment of a potential as the concentration of the corresponding ions in solution on the other side of the interface. For every tenfold decrease in hydrogen gas pressure, the potential of a hydrogen electrode becomes more electropositive by 0.029 volt. Conversely, for every tenfold decrease in oxygen pressure, the potential of an oxygen electrode becomes less electropositive by 0.015 volt.

As has been previously mentioned, the potentials of the electrodes listed in Table 1 are based on the assumption that the gas electrodes are at

Table 1.—The Electromotive Force Series (25° C.)

Electrode	Reaction	Potential (E_h)
Gold	$Au, \rightarrow Au^{+++}$	$+1.36$
Chlorine	$\frac{1}{2}Cl_2, \rightarrow Cl^-$	$+1.358$
Silver	$Ag, \rightarrow Ag^+$	$+0.798$
Oxygen	$\frac{1}{2}O_2, \rightarrow OH^-$	$+0.400$
Copper	$Cu, \rightarrow Cu^{++}$	$+0.344$
Hydrogen	$\frac{1}{2}H_2, \rightarrow H^+$	± 0.000
Lead	$Pb, \rightarrow Pb^{++}$	-0.12
Tin	$Sn, \rightarrow Sn^{++}$	-0.14
Nickel	$Ni, \rightarrow Ni^{++}$	-0.231
Cadmium	$Cd, \rightarrow Cd^{++}$	-0.401
Iron	$Fe, \rightarrow Fe^{++}$	-0.441
Zinc	$Zn, \rightarrow Zn^{++}$	-0.762
Aluminum	$Al, \rightarrow Al^{+++}$	-1.69

atmospheric pressure, and that the environment in all cases contains in effect one atomic weight in grams of ions of the element involved in 1000 grams of water. In this form the e.m.f. series is of little value in corrosion studies. To be useful it must be modified to meet the conditions of each individual problem. For example, let it be assumed that pure water is the corrosive environment. Pure water is known to be one-ten millionth normal * in hydrogen ions and to contain an equal concentration of hydroxyl (OH) ions. Since the concentration of each of these ions in water is seven tenfold changes from normal, the potential of the hydrogen electrode (at atmospheric pressure) in water is not zero as in Table 1 but 7×0.059 volt or 0.413 volt more electronegative (more anodic) than zero. In like manner, it can be calculated that the potential of the oxygen electrode at atmospheric pressure in water is not +0.400 volt, but +0.400 volt plus 7×0.059 volt, or +0.813 volt. The difference in potential between the hydrogen and oxygen electrodes (at atmospheric pressure) in water is therefore the difference between −0.413 and +0.813 volt, or 1.23 volts. This figure is a very convenient one to remember because, as can readily be calculated, it is a constant which is unaffected by the presence of dissolved salts, acids or alkalies. In other words, the difference in potential between the hydrogen and oxygen electrodes (at atmospheric pressure) in any aqueous environment is invariably 1.23 volts. (This theoretical value of 1.23 volts is never attained in practice owing to irreversible processes at the oxygen electrode.) For example, if sufficient acid were added to pure water to change it from pH 7 to pH 6, a tenfold increase in hydrogen ions and a tenfold decrease in hydroxyl (OH) ions would occur, and the potential of the hydrogen electrode would change from −0.413 volt to −0.354 volt, and the potential of the oxygen electrode from +0.813 volt to +0.872 volt. Thus the electrode potentials would be shifted simultaneously in the same direction and would still remain 1.23 volts apart.

The relationships which exist between the potentials of hydrogen and oxygen electrodes at any pressure up to atmospheric in environments ranging in acidity from normal in hydrogen ions (pH 0) to normal in hydroxyl ions (pH 14) are given in Figure. 2.[7] It will be noted that the reference zero of the potential scale in this diagram is identical with that employed in Table 1.

An atmospheric pressure hydrogen electrode can be established by bubbling hydrogen gas over a relatively inert or noble metal, such as platinum, which hydrogen readily permeates, or by impressing upon it just sufficient voltage to discharge hydrogen in the form of gas bubbles. Oxygen electrodes can be formed in an analogous manner with oxygen. In the corrosion process hydrogen electrodes are established on the

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* That is, in effect one atomic weight in grams of hydrogen ions per liter of solution. For practical purposes this does not differ significantly from one atomic weight in grams of hydrogen ions in 1000 grams of water.

[7] Adapted from Clark, W. M., "Determination of Hydrogen Ions," 3rd ed., p. 387, Baltimore, Williams and Wilkins Co., 1928.

cathodic areas of the corroding metal by electrolytic action. The effective pressures of the hydrogen electrodes so formed may vary from almost zero to one atmosphere and even more, depending upon the relative rates of hydrogen discharge and hydrogen removal at the cathode surface. The

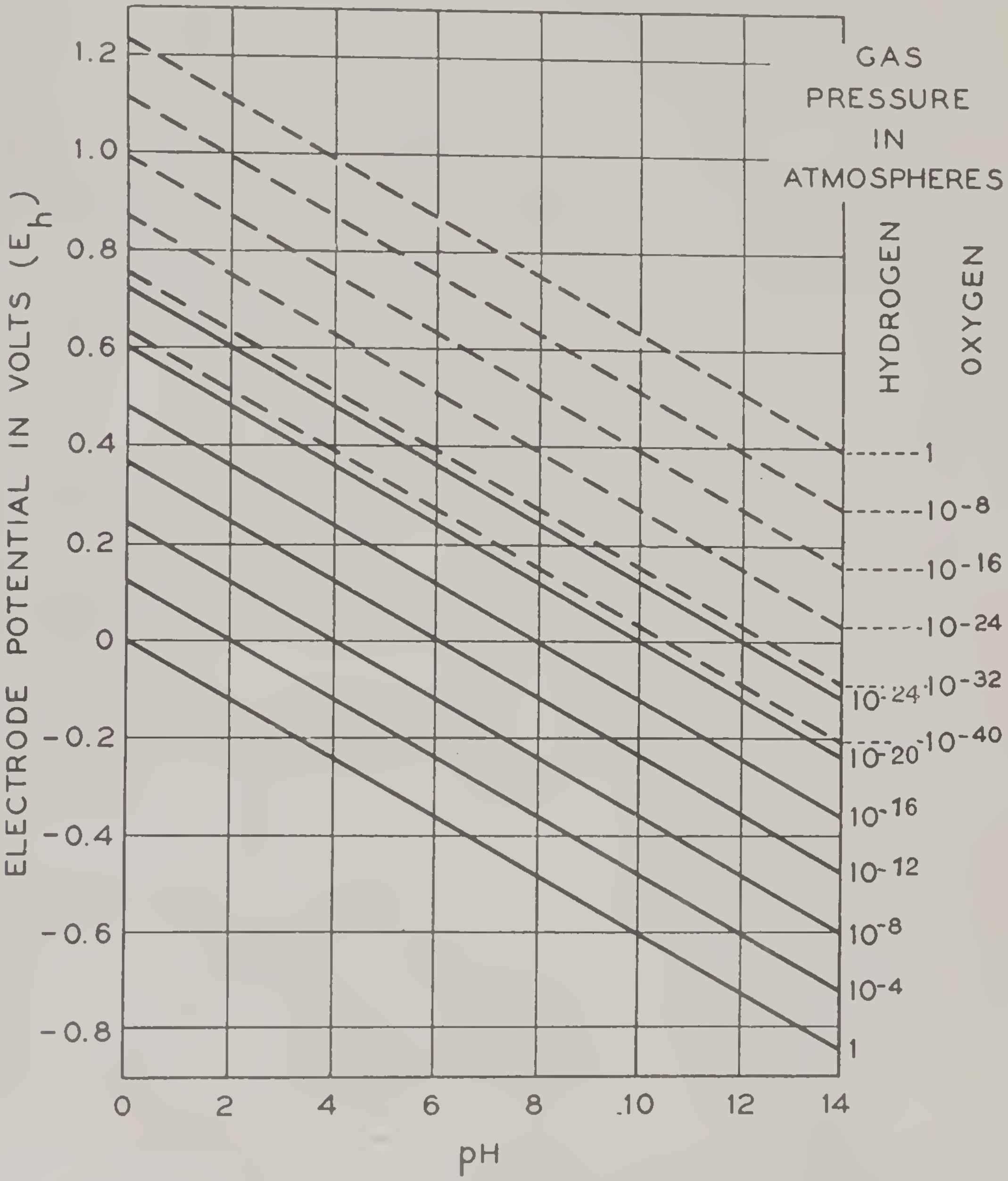

Figure 2.—The Relationship between the Potentials of Hydrogen and Oxygen Electrodes at Various Pressures and Acidities.

rate of hydrogen discharge is determined primarily, of course, by the driving force of the corrosion reaction, as indicated by the e.m.f. series. The rate of hydrogen removal from the cathode surfaces is determined by the rate of its diffusion away from the interface and by the concentration of oxygen which may be present at the interface. If the concentration of oxygen is more than sufficient to combine with all the hydrogen liberated, the cathodic areas are in reality functioning as oxygen electrodes. Theoretically, the maximum pressure which could be reached by such an oxygen electrode would be 0.21 atmosphere, the pressure of oxygen in air. The discharge of hydrogen gas below atmospheric pressure or the bubble point in the absence of the oxygen may be compared to the evaporation of water below the boiling point. Extending this analogy, the discharge of hydrogen on an oxygen electrode may be compared to the evaporation of water below the boiling point under reduced pressure, and the evolution of hydrogen gas bubbles corresponds to actual boiling of water.

It is now of interest to consider the electrochemical behavior of a metal electrode when immersed in a definite volume of pure water. Initially there are no metal ions in solution. It follows from the discussion that has preceded that the potential of the metal against its environment at the *instant* of immersion must be infinitely electronegative or in other words, the initial corrosion tendency is infinitely great. In consequence, hydrogen ions are forced out of solution on the cathodic areas, being replaced by the metal ions passing in at the anodic areas. The interfacial reactions involved take place with a speed approaching that of light, and within a fraction of a second after immersion the metal ion concentration at the surface of the anodes has passed through a sufficient number of tenfold changes to bring the potentials of all areas of the electrode surface well within the range of the e.m.f. series as usually defined.

Simultaneously with the increase in metal ion concentration, the hydrogen ion concentration decreases and the hydrogen pressure at the cathodic areas increases. The result is that the potentials of the metal and of hydrogen approach each other and may become and remain identical, under which circumstances corrosive action must cease. This may more readily happen, and with a minimum of corrosion, in a closed system, which permits the development of appreciable hydrogen pressures and consequently the maintenance of fairly electronegative cathode potentials. It may also happen in an open system (in the absence of oxygen) with the more electropositive metals, such as copper and silver. In these cases only an infinitesimal amount of corrosion is necessary to develop and maintain hydrogen electrodes of sufficient pressure to equal the anodic areas in potential. As a rule, however, metals cease corroding merely because their environments have become saturated with them before equality of the potentials of the anodic and cathodic areas is attained. This holds true not only for the more readily corrodible metals, such as zinc, iron and lead, but also for the semi-noble metals, if oxygen is present. If the diffusion of metal ions from the surface of a corroding metal is slow, corrosion may cease when only the environment immediately adjacent to the metal has become saturated. Protective films so formed result from the precipitation of metal ions as hydroxides or other, more insoluble compounds, in such close proximity to the metal surface that further corrosive action is retarded or possibly even prevented entirely. Such precipitation may be due solely to a paucity of aqueous environment. For example, a thin film of moisture on a metal surface may be rapidly converted by corrosion and evaporation, first to a saturated solution of the metal hydroxide, and then to the dry hydroxide or oxide. Subsequent similar wettings may serve to render the film of corrosion products thicker and more impervious. Obviously the oxygen, carbon dioxide and in some instances other gases in the environment may aid in precipitating the metal ions with the result that there may be developed a coating which is resistant to the solvent action of water.

This coating may be of such nature as to render the metal surface passive or, in effect, noble. Chromium does not readily corrode because it has already corroded so rapidly and so uniformly that the film of corrosion product formed does not mar its reflectivity. The electrochemical behavior of chromium indicates that its surface is not chromium but oxygen in some form. It seems entirely probable that the passive film consists of either a continuous layer of adsorbed oxygen or a continuous layer of closely packed chromic oxide, with each molecule so oriented that the oxygen is on the outside. Similarly in the case of iron it has been shown that passivity is associated with an oxide film. Electron diffraction studies indicate that this film when formed in air is composed of ferric oxide of a close packed structure in contrast to a film of ferrous hydroxide which is not so protective. In solution it seems likely that the degree of passivity of the iron surface is a function of the concentration of oxygen on the surface, and that the composition of the passive film may correspond to that of a definite oxide in which an indeterminate amount of oxygen may be dissolved depending upon the circumstances.

Thus far the discussion of corrosion mechanism has pertained to the origin of corrosion cells, their potentials and the function of corrosion products in determining the endpoint of the process. The rate of corrosion, that phase of the problem of most practical importance, is more complex. As previously stated it cannot be calculated but must be measured in some manner. The preferable experimental approach would be to measure the characteristics of individual corrosion cells, since the current which flows in these cells in a given time is a direct measure of rate of corrosion. While it is infeasible to do this, it is possible to determine the relative importance of those factors which increase and those which decrease the rate of corrosion.

The great speed of the primary electrode reactions has been referred to previously. Although metal ions dissolve and hydrogen ions are discharged at extremely high speeds, the secondary processes of diffusion and convection by means of which metal ions are removed from the proximity of the anode are relatively slow. As a consequence, the concentration of metal ions immediately adjacent to the anode is considerably higher than that which would exist if the solution remained uniform throughout, and the tendency for metal to dissolve in the film of solution at the anode surface is less than it would be if the solution were uniform throughout. This difference in solution tendency expressed in volts is known as anode polarization. In like manner, the decrease in hydrogen ion concentration at the cathode and the accumulation of discharged hydrogen at its surface gives rise to cathode polarization. Gas polarization, usually referred to as "overvoltage," is entirely analogous to metal polarization, with the exception that concentration of the product of electrolysis *within* the electrode is much more significant. It is obvious that polarization must increase with current density and, to a much lesser extent, with time. Polarization is a counter-electromotive force which invariably opposes the causative voltage.

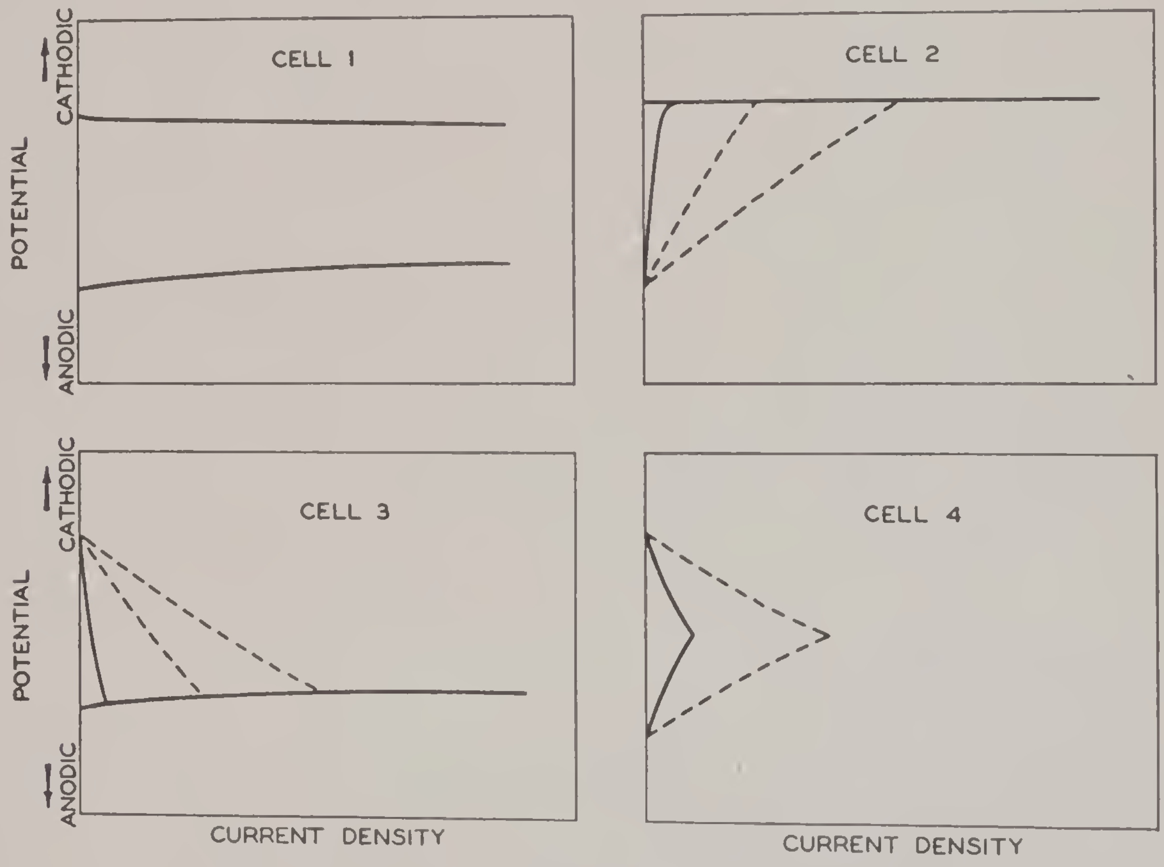

Figure 3.—Types of Polarization in Corrosion Cells.

This polarization behavior of corrosion cells largely determines the rate of corrosion. It is obvious that the effective voltages of corrosion cells may be reduced by polarization virtually to zero, in which case the rate of corrosion is limited to that required to maintain this polarization. In other words, the progress of corrosion may be controlled by the extent either of anode polarization or cathode polarization or both. Figure 3 represents the variety of current density-potential relationships which may exist in corrosion cells.[8] In Cell 1, in which there is no appreciable polarization of either anodic or cathodic areas (as indicated by the small change of potential with current), corrosion current flow is limited by the resistance of the electrolytic paths between anodes and cathodes; and since this may be small if these areas are contiguous, the corrosion rate may be high. In Cell 2 the anode is highly polarized as represented by the solid line, or progressively less polarized as the point of intersection with the nonpolarized cathode occurs at higher and higher current densities, as represented by the dotted lines. In a similar way Cell 3 shows cathode polarization only and Cell 4 both anode and cathode polarization. Since the rate of corrosion is proportional to the flow of current per unit area it is obviously limited in the last three cases by the values of current density at which the polarization curves intersect. In the presence of adequate oxygen concentration or in cases where hydrogen is readily discharged, corrosion cells are likely to resemble Cell 1. Where this is not the case, as in the absence of oxygen or where the cathodes have high values for hydrogen overvoltage, the result will be as shown for the cathodically polarized Cell 3. The presence of an inhibitor such as a positively charged colloid or the amalgamation of the metal surface with mercury are other conditions which promote cathode polarization. On the other hand, the action of passivating agents such as chromates, silicates and in some cases sulfates, carbonates, etc., is to produce anodic polarization as in Cell 2. It will be observed that, whereas in the presence of inhibitors of the type mentioned above which polarize the cathode, the resulting potential of the corrosion cells and therefore of the metal specimen as a whole should move in the anodic direction as the process of inhibition takes place, in the case of passivating agents (which influence anode processes) the effect of increasing passivation is a trend of potential in the cathodic or noble direction. In both cases corrosion is retarded or prevented entirely. It is well to point out, however, that if the concentration of the passivating anion is inadequate to insure and maintain complete passivity there may be small insufficiently protected areas at which metal will dissolve, giving rise to pitting.[9] These areas may be so small as not to affect appreciably the composite potential of the metal under the conditions of measurement.

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[8] Burns, R. M., *Bell System Tech. J.*, 15, 20 (1936); see also, Evans, U. R., *J. Franklin Inst.*, 208, 45 (1929).

The manner in which the conductance of the surrounding electrolyte influences the rate of corrosion is illustrated in Figure 4A, in which the upper curve represents the cathodic and the lower the anodic polarization. Assuming equal anodic and cathodic areas the corroding current density for the lower conducting solution is represented by *M* and that for the higher conducting solution by *N*. In the actual case where anodes and cathodes are in close juxtaposition, the internal resistance is low and consequently the corroding current density approaches that represented by the intersection of the polarization curves.

Thus far consideration has been confined for the sake of simplicity to corrosion cells in which the anodic and cathodic areas are equal. Usually in actual experience this is not the case. In corrosion characterized by pitting, the anodic area is generally small compared to the cathodic areas. This situation is illustrated in Figure 4B, in which it will be seen that under these conditions a high corroding current density corresponding to a rapid rate of attack may occur. Conversely, in cases where the ratio of anode areas to cathode areas is large, the rate of attack per unit area will be slow, being thus controlled by cathodic polarization.

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[9] Mears, R. B., *Discussion Trans. Electrochem. Soc.*, 69, 181 (1936).

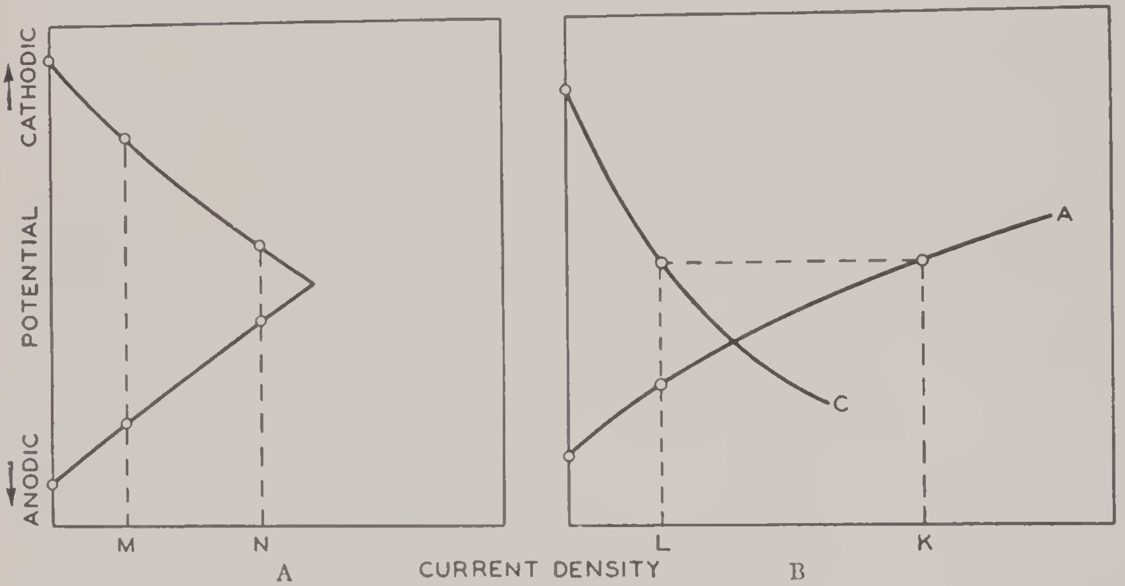


Figure 4.—Effect of Conductance and of Electrode Area on Corrosion Current Densities.

M = Lower Conducting Solutions.
N = Higher Conducting Solutions
L = Corrosion Current Density for Cells of Equal Cathode and Anode Areas.
K = Corrosion Current Density When Ratio Anode Area to Cathode is Small.

In this connection it may be of interest to consider the effect of impurities upon rate of corrosion. If the contaminating metal is anodic and exists as a separate phase it will tend to dissolve with the formation of small pits which, having once formed, may possibly continue to function as the anodes of oxygen concentration cells. If, on the other hand, the metallic impurity is cathodic and is present as a separate phase, corrosion will be rather more uniform in character, and its rate will be controlled in the absence of oxygen by the ability of the impurity to discharge hydrogen. Unless its overvoltage is low, that is, unless it discharges hydrogen readily, the rate of corrosion will be slow, the corrosion cells being polarized cathodically. The presence of oxygen or oxidizing agents under these conditions will depolarize these cathodic areas and accelerate corrosion.

From the foregoing it is apparent that a knowledge of the anodic and cathodic current density-potential relationships which are established on the surface of a metal in a given environment would make possible an understanding of the processes which are taking place and lead to a prediction of corrosion behavior. It is generally impossible to measure these quantities as they relate to individual corrosion cells, owing to a lack of knowledge of the electrode areas involved. By ingenious laboratory methods this can be done in certain cases however.[9a] Probably these electrode areas vary widely in size, and change in size with the progress of corrosion. Sometimes the nature of the cathode is also uncertain. Practically, however, it is a simple matter to determine a composite of the resultant potentials and their change with time. These time-potential measurements indicate whether the process is anodically or cathodically controlled and in some cases furnish information as to the rate at which it is proceeding, experimental facts which are of value in predicting corrodibility.[10] A recording potentiometer is of considerable assistance in this connection.

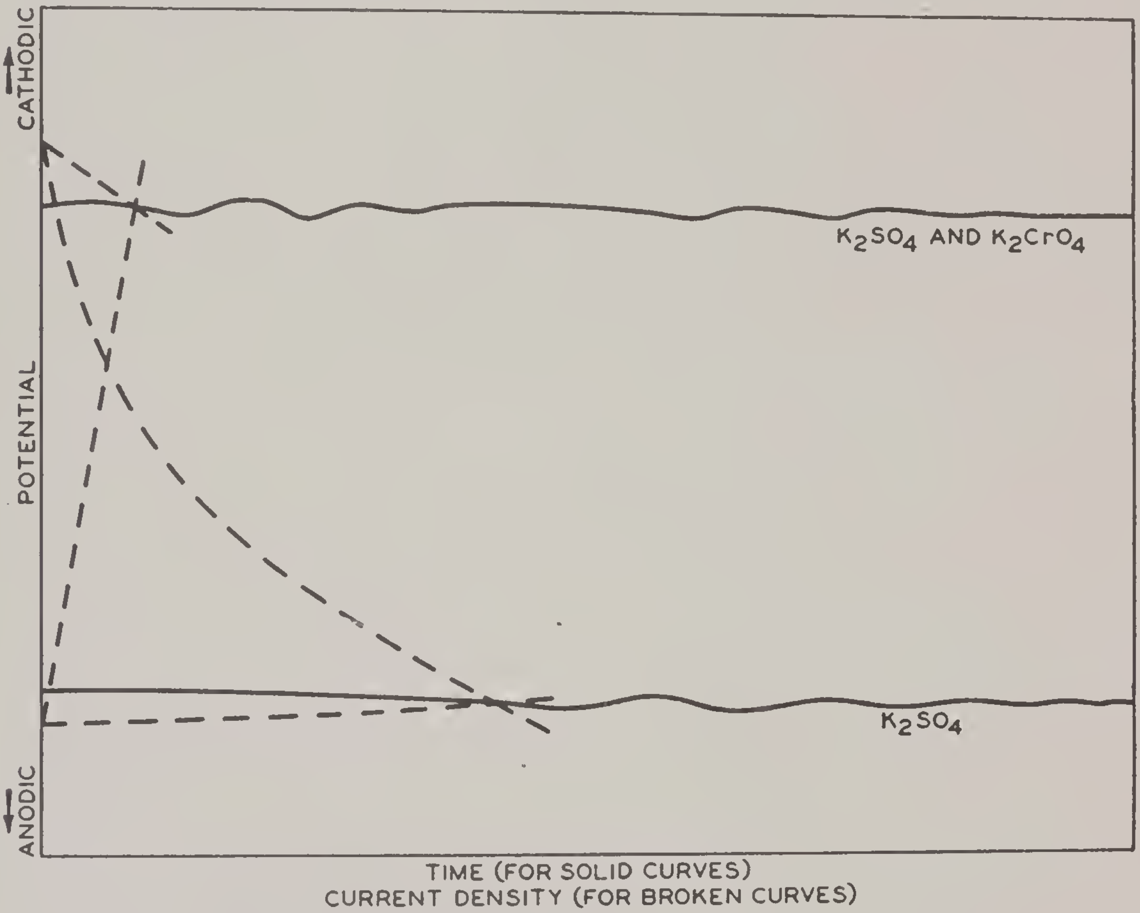


Figure 5.—Time-Potential Relationship of Iron in K_2SO_4 as Affected by Addition of K_2CrO_4.

Figure 5 illustrates schematically the correlation between these time-potential relationships and the anodic and cathodic polarizations which determine their positions. It will be seen that the potential of iron in a solution of potassium sulfate (represented by the lower solid curve) is essentially the potential of iron in the solution, the cathodic areas being polarized. When potassium chromate is added to the solution the resultant potential of iron is shifted markedly in the cathodic direction, the position being determined by anodic polarization. The actual values of the potential of iron in these cases are of the same order as that of iron alloyed and rendered passive by the addition of chromium and nickel.

[9a] Brown, R. H. and Mears, R. B., *Trans. Electrochem. Soc.*, Preprint 74-2 (1938).

[10] May, R., *J. Inst. Metals,* **40,** 152 (1928); Bannister, L. C. and Evans, U. R., *J. Chem. Soc.*, 1363 (1930).

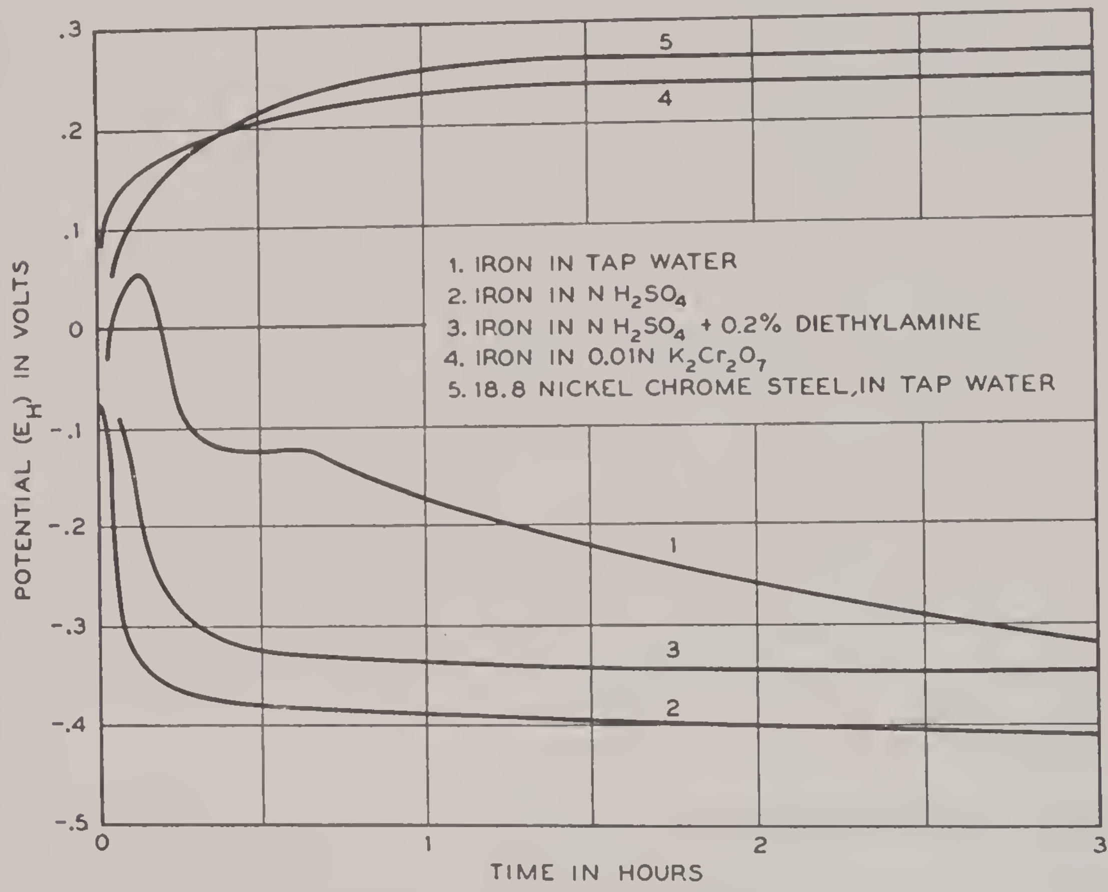


Figure 6.—Potentials of Iron and Stainless Steel in Water and Certain Solutions.

In Figure 6[11] is shown the actual time-potential behavior of specimens of iron and 18-8 chromium-nickel steel immersed in water and certain solutions. It will be observed that the potential of iron in normal sulfuric acid rapidly becomes electronegative. The initial trend of a similar specimen immersed in tap-water is toward the noble side, owing probably to the passivity of the air-formed film. Within a few minutes, this trend is reversed, the specimen becoming more electronegative probably because of the destruction of this film. In the presence of an oxidizing solution, potassium dichromate, it will be seen that the potential of iron (represented by curve 4) becomes markedly electropositive. A similar passive behavior is shown by stainless steel in tap-water (curve 5). The iron specimens,

[11] Burns, R. M., *J. App. Phy.*, 8, 398 (1937).

the potentials of which are represented by curves 1 and 3, displayed active corrosion, but iron in potassium dichromate solution (curve 4) and stainless steel in water did not corrode. In other words, a trend in the electronegative direction, which as mentioned before is characteristic of cathodic polarization, is associated with active corrosion, whereas the electropositive trend of potential is indicative of passivation. It is of interest to note in this connection that certain organic compounds used as corrosion inhibitors which, as previously mentioned, function by retardation of the cathodic reaction, appear to have little or no influence on the characteristic of time-potential curves. The experiment represented by curve 3, for example, differs from that of curve 2 only by the presence of 0.2 per cent diethylamine, a typical corrosion inhibitor. Corrosion has been greatly retarded in this case but the iron is still in the active or corroding class.

The foregoing discussion of the principles of corrosion has outlined the mechanism by which metals corrode. Later chapters will seek to apply these principles in more detail in discussions of the performance of coatings of various kinds. Detailed discussion of methods of measuring rates of corrosion is given in Chapter 12. It will be evident in discussing metallic coatings that insofar as these coatings are continuous the behavior of the coated surface will be practically identical with that of the coating metal in solid form. When, as is more often the case, the coating contains or developes pores, galvanic couples of dissimilar metals arise. In terms of these couples, metallic coatings fall into two general classes: those in which the coating metal is the anodic member of the couple, as in the case of zinc coatings on iron and steel, and those in which the coating metal is cathodic, as illustrated by copper, lead, and in some cases, tin coatings, on ferrous metals.[11a]

Anodic coatings protect the basis metal by changing exposed areas of it from anodes to cathodes; in accomplishing this result dissolution of the coating occurs. This sacrifice of the coating may continue until its complete dissolution. Before that point is reached it will be observed that the portions of the exposed basis metal most remote from the disappearing coating metal will begin to corrode. In other words there is a limit to the size of the area which, under given conditions, will receive cathodic protection; beyond that limit local corrosion cells begin to function.

Considerable attention has been given in recent years to the use of cathodic protection for the preservation of large structures such as pipe lines, boilers and lead-sheathed cables, and some reference will be made to this in a later chapter. The subject has received theoretical treatment by several investigators.[12]

[11a] For a lucid discussion of the anodic-cathodic relationship of metallic coatings, see Hoar, T. P., Paper before Electrodepositors' Tech. Soc. (London), Oct. 20, 1937.

[12] Jensen, C. A., *J. Soc. Chem. Ind.*, 15, 547 (1896).
Bauer, O., and Vogel, O., *Mitt. Kgl. Materialprüfung*, 36, 114 (1918).
Evans, U. R., and Stockdale, J., *Metals and Alloys*, 1, 377 (1930).
Evans, U. R., *Metals and Alloys*, 2, 62 (1931).
Mears, R. B., and Brown, R. H., *Trans. Electrochem. Soc.*, 74, (1938).

Coatings of metals which are cathodic to the basis metal may show pinhole corrosion, each pore becoming a pit which penetrates, and may in time perforate, the basis metal. It is for this reason that every effort is made in the production of this type of coating to secure a non-porous metal layer. The highly protective character of such coatings when pore-free is attributable, as mentioned earlier, to the corrosion resistant quality of the superficial films which develop upon their surfaces.

Organic coatings act as physical barriers which exclude more or less effectively the corrosive elements of the environment from the metal surface. Both moisture and oxygen permeate the coating, however, with the result that the basis metal may corrode. As will be shown, various surface treatments of the metal, such as phosphating and the use of inhibitive pigments, may retard or even prevent corrosion for considerable periods of time.

Chapter 2

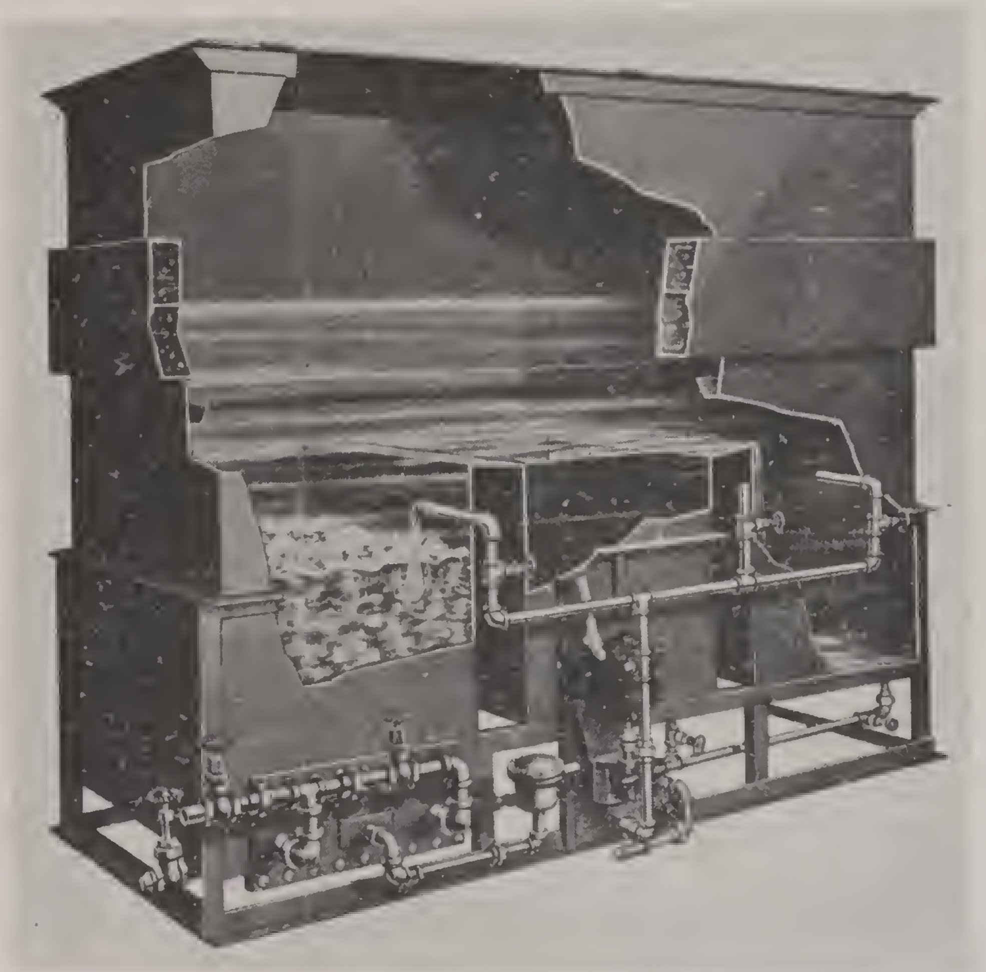
Surface Preparation for the Application of Coatings

The chemical and physical nature of a metallic surface has a very marked effect upon the quality of any coating applied to the surface. It is well known that the presence of grease, corrosion products, dirt, and extraneous materials affects the adherence and continuity of coatings whether of metallic or organic nature. The physical structure of the surface influences the adhesion, and, in the case of metallic coatings, the porosity, uniformity, and smoothness of the coating. In general, it may be said that the character of a coating is no better than the surface to which it is applied, and consequently it has come to be recognized that the production of protective coatings of high quality is dependent upon the proper and thorough pretreatment of the surface of the basis metal.

The preparation of a metal surface for coating may involve three steps. There is first the removal of grease and other contamination, usually followed by a pickling or sand or shot-blasting operation to remove oxide scale and corrosion products, and finally, in some cases, an etching, graining, polishing or buffing treatment may be employed to secure adhesion or to obtain appearance characteristics desired in certain metallic coatings. A great variety of practices has arisen to accomplish these ends and the choice of the procedures which are employed is determined largely by the character and volume of the work to be finished and the economics of alternative processes in given localities. A general outline of surface preparation methods will be given here, and further details of some of the processes will appear later in connection with the application of specific coatings.

Metal parts, upon reaching the finishing department, are nearly always contaminated with grease derived either from slushing oils employed for temporary protection during storage or from cutting or buffing compounds used in drawing, machining, threading and surfacing operations. In other cases lubricating oils and greases, together with soot and dirt, may be the principal type of surface pollution. The oily substances fall in general into two classes, animal or vegetable fats and mineral oils. The former are removable upon saponification with strong alkalies, while the latter class is effectively removed by emulsification with soaps, soap substitutes, such as the alkali salts of sulfonated naphthalene or higher alcohols, and other substances capable of reducing the surface tension of water. Many organic solvents dissolve both classes of oily substances.

An important new development in solvent degreasing[1] is the use of chlorinated hydrocarbons, notably trichlorethylene, under conditions in which the vapors are allowed to condense on the surface to be cleaned, removing thereby the greasy materials in the drip of the condensate. The use of petroleum-base solvents has been rather limited, owing to the fire hazard involved, and the fact that objectionable amounts of grease remain on the surface after removal of the work from the solvent. These limitations are avoided in the use of trichlorethylene vapor. The process, moreover, is well adapted to automatic operation. While the equipment for carrying out the process consists essentially of a heating chamber for the liquid, a vapor compartment (in which the work is cleaned) and a condenser, in the form of cooling coils, for controlling the vapor level in the apparatus, it has been found advantageous in many cases to include pro-



Courtesy of Detroit Rex Products Company.

Figure. 7.—Three-dip trichlorethylene degreaser which gives straight-line sequence of cleaning operations, consisting of immersion in boiling solvent, immersion in clean cooling rinse, and final vapor rinse.

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[1] Davidson, W. W., *Trans. Electrochem. Soc.*, **72**, 413 (1937).

vision for immersion in the liquid solvent before exposure to the vapor. There is shown in Figure 7 [2] a cut-away view of a three-stage trichlorethylene degreaser of the type now being widely used in industry.

In the operation of the three-dip degreaser, the work passes on suitable conveyors into the boiling solvent, where the bulk of the grease is removed, then into a chamber of cold purified solvent, and finally through solvent vapor. The condensate from the condenser is fed back into the reservoir which supplies the chambers with liquid solvent, thus continually purifying the liquid. The speed of the conveyor is usually from 6 to 8 feet per minute. In cases where conveyor operation is not justified, the work may be hand-dipped, employing baskets or racks.

Immersion in hot alkaline solution is the most common method of cleansing metal surfaces. It is made more effective by the application of current, making the parts to be cleaned cathodic. Under such conditions, high concentrations of free alkali are maintained at the surface, and the copious evolution of hydrogen causes agitation and aids in the emulsification of the oily substances present. Electrolytic cleaning of this type has been extended recently to the strip metal industry as a means of removing rolling oils from strip to be used in the manufacture of tin-plate.[3] In this process, coils of 5000 feet of strip, 36 inches wide and 0.010 inch in thickness are degreased at rates up to 900 feet per minute, employing a hot solution of the ortho- and meta-silicates of sodium and a current density of about 1 ampere per $dm.^2$ (10 amperes per sq. ft.)

There is considerable variation in cleaning procedures. In some cases the work is dipped in one hot alkaline solution and electrocleaned in another solution. The work is sometimes made anodic for a portion of the time in the electrolytic cleaner.

Soda ash is one of the principal constituents of most alkaline cleaners. Caustic soda is added in small amounts to saponify fatty substances, and soaps are widely used where the oil to be removed is of the mineral type. Sodium phosphate, borax, and sodium silicate are further examples of suitable reagents for metal cleaning.

The removal of oxide scale is accomplished either by acid pickling or by mechanical abrasion of the surface. The pickling operation consists in immersing the metal in dilute acid until the mill scale has been loosened or dissolved. The usual practice is to use from 4 to 5 per cent sulfuric acid at about 65 to 75° C. (149 to 167° F.), although hydrochloric acid of various concentrations is employed to a limited extent. Inhibitors are used, particularly with sulfuric acid, to minimize the attack of the acid upon the metal. These are usually organic substances, such as glue, pyridine, and sulfonated oils, which, as is stated in a more extended discussion in Chapter 4, appear to restrain dissolution of the metal by inducing cathodic polarization.

[2] Courtesy of the Detroit Rex Products Company, Detroit, Michigan.

[3] Stone, M., *Metal Cleaning and Finishing,* 9, 988 (1937); 10, 20 (1938).

An initial dip in hydrofluoric acid is sometimes used in pickling sand castings. A variety of scaling or acid dips is employed for removing tarnish and oxide from brass and bronze. These are usually mixtures of sulfuric and hydrochloric acids containing small proportions of nitric acid.[4]

For the preparation of iron and steel surfaces for painting it has been found advantageous to pickle in phosphoric acid solutions.[5] Owing to the cost of this acid, the more usual practice is to descale first in sulfuric acid and follow by a dip in 2- to 10-per cent phosphoric acid containing usually a fractional per cent of iron. The priming paint is applied directly to the phosphated iron surface. It is not common practice to pickle structural steel.

Anodic pickling is employed to a certain extent as a means of increasing the rate of pickling and at the same time of bringing about a mild etching of the metal surface suitable for the application of heavy electrodeposited coatings. In this case a 25- to 30-per cent solution of sulfuric acid is suitable, employing about 150 amperes per sq. ft.[6]

Sandblasting has long been a favorite method of oxide removal, particularly where a slightly roughened surface is desired for the improvement of adherence of coatings. Steel grit and shot have replaced sand to a considerable extent as abrasives. In operation, the abrasive is introduced into an air stream at air pressures of from 25 to about 100 pounds per sq. in., and the blast directed over the metal surface until the oxide scale is removed. In automatic conveyor type machines for blasting, the nozzles are so arranged as to provide a more or less uniform blasting of the surfaces of the parts. The process of blasting is said to induce a certain amount of surface hardening. A comparison of the relative roughness of the surface produced by blasting with various sizes of steel grit is shown by means of profilographic records in Figure 68 in Chapter 14.

A widely practiced method of scale removal from stock which has undergone weathering is by scratch-brushing with wire brushes, either hand or machine operated. Weathering serves to loosen mill scale by under-rusting. A fairly uniform, finely scratched surface may be produced upon metals by this means. The rotating wire brush method has recently been investigated in some detail.[7] It was found that it is possible to remove hard scale from a steel surface provided the steel wire of the brush is hard enough, of proper size, and provided considerable pressure is applied. Under certain conditions of operation the mill scale was merely burnished. It is an impractical method of descaling unless the surface has been previously weathered.

A grinding operation employing a solid wheel of hard, relatively coarse abrasive, either silicon carbide or fused alumina, is sometimes used to remove hard mill scale. This method is also in common use as a means of removing fins, burrs, and machine marks on fabricated parts.

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[4] Graham, A. K., *Trans. Am. Electrochem. Soc.*, 52, 289 (1927).

[5] Footner, H. B., Corrosion Committee of Iron and Steel Institute, Fifth Report, p. 369, 1938.

[6] Hall, N., *Monthly Rev. Am. Electroplaters' Soc.*, 24, 905 (1937).

[7] Corrosion Committee of Iron and Steel Inst., Sec. E3, p. 355 (1938).

Polishing and buffing are employed for the production of uniform smooth surfaces where it is desired to obtain electroplated coatings with such characteristics. These operations may be used also for surface finishing as, for example, on nickel coatings before the application of chromium, or as a finish for brasses, bronzes, etc. Still another process used mainly to remove surface roughness and to produce a luster on metal parts and metal-coated parts is ball burnishing. This is carried out in a rotating barrel using hardened steel balls, jacks or cones and a special soap solution.

Polishing and buffing are somewhat similar operations, the second following the first where high luster or color is desired. Both processes employ revolving wheels. Polishing wheels are made from felt, walrus hide, leather, sewed cotton buffs, etc., which are coated on the outside surfaces beforehand with abrasives, such as emery, corundum or fused alumina, held in position by glue.[8] Solid discs of wood or metal, over which is slipped a sleeve faced with abrasive, comprise another type of polishing wheel. Lubricants may be used in polishing with wheels of either kind.

Buffing wheels are generally composed of sewed cloth or canvas. The abrasive in this case is not a part of the wheel, but is applied to the wheel intermittently from a bar or cake containing its own binder, which may be rosin with tallow or petrolatum. Among popular abrasives for buffing are tripoli (largely silica from the weathering of quartz-bearing rock), rouge and crocus grades of ferric oxide, pumice, Turkish or American emery, whiting and Vienna lime (calcined dolomitic limestone).

[8] Garner, C., *Monthly Rev. Am. Electroplaters' Soc.*, 25, 96 (1938).

Chapter 3

Types of Metallic Coatings and Methods of Application

HISTORICAL

Man has devised many methods of coating one metal with another. The ancients plated and inlaid base metals with gold, silver, and a mixture of the two known as electrum. These noble-metal coatings appear to have been hammered over the surfaces of bronze, copper or iron which were previously heated. The elder Pliny described "fire gilding" employing gold amalgam. The Romans coated copper vessels with tin, probably by immersing them in the molten metal. Coating sheet-iron with tin is of much more recent origin, although it was a well established art for a century before the appearance of hot-dipped zinc coatings about 1740. Sheffield plate, produced by fusing sheet silver on copper or brass, was discovered about 1743 and for a hundred years was a prosperous industry, finally being largely superseded by electroplating. Gold and silver plate of this type are now made by soldering or welding the coating to the base metal. Coating metals with gold leaf and gilding with gold powder suspended in a liquid are old arts. The early electroplating operations were of the "dip-gilding" type in which base metals, immersed in solutions of gold, silver or platinum salts, become coated with very thin films of the noble metal by replacement. This process is still widely used in the production of cheap jewelry. Another type of contact plating described in a reference book for "the manufacturer, tradesman, amateur and heads of families" [1] consisted in zincing or tinning copper and brass vessels by boiling them respectively in solutions of zinc salts containing zinc turnings or tin salts containing tin turnings. Following the invention of the voltaic cell electroplating in the modern sense came to be practiced. Silver, gold and zinc were first electrodeposited in 1840 and platinum in the next year. Later copper, nickel, tin and lead and finally most of the common metals except aluminum and magnesium have come to be electroplated as firmly adhering coatings from aqueous solutions.

Since the beginning of the present century a number of new metal coating processes have been devised. Of these, the most important commercially are cementation, metal spraying and "metal-cladding." Cementation is a means of surface alloying and finds numerous metallurgical applications which depend upon the modification of the surface of a metal, the most familiar of which is the important process of "case hardening" of steel. Other examples are "sherardizing" in which the surface of an iron article is zinc-coated and "calorizing" in which the coating is aluminum. Metal-spraying consists in atomizing molten metal by compressed air or by some mechanical device, forcing it through a nozzle at high velocity and allowing the resulting spray to impinge on the surface to be coated. Most of the common metals and alloys can be sprayed, but zinc, tin, aluminum, copper, lead, iron and brass have been used to the greatest extent. Almost any desired thickness of coating may be obtained by this process. "Metal-cladding" is a term used to describe the method of coating one metal with another by rolling the two metals in intimate contact with each other. Coherence of the two metals is induced either by soldering, electro-welding, or casting one in contact with the other previous to the rolling operation. By this mechanical process steel for example is coated with copper, nickel or with alloy steels.

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[1] Cooley, "Cyclopedia of Practical Receipts," 532, 576, New York, Appleton & Co., 1846.

Two other metal coating processes to attain limited commercial application recently are dependent upon the condensation of metal vapor in a partial vacuum. In cathode sputtering, the more widely used of the two, the coating metal is evaporated from the cathode during a glow discharge induced in a chamber at a pressure of 0.01 to 0.1 mm. of mercury and a voltage of from 500 to 2000. In the other process the coating metal is vaporized by heating it in a vacuum of 10^{-4} mm. of mercury. In both processes condensation of the metal vapor usually occurs on the walls of the chamber as well as upon the surface to be coated.

Immersion in Molten Metal: "Hot-Dipping"

One of the oldest and most familiar of the commercial processes of applying metallic coatings to other metals is that known as "hot-dipping." Essentially this process involves immersing bodily the article to be coated in a bath of molten metal for a short time; usually very little, if anything, additional is done to change the properties of the metal coating which adheres to the surface upon removal of the article from the molten metal bath.

Principles

For the successful coating of one metal with another by means of the hot-dipping process, it is necessary that the two metals alloy with each other, at least to some extent. A clean glass rod when dipped into water and withdrawn is found to be covered by an adhering film of moisture, the force of surface tension serving to make this film uniform over the surface which was wetted. The production of a metal coating by immersion in a bath of molten metal is not strictly analogous to this simple illustration, however, but is more like the case of the immersion of a crystal of rock salt in water. The film which covers the surface in this case is not one of pure water, but contains an appreciable proportion of the salt in solution. Because of the tendency of the substance to dissolve, it is decidedly easier in this case to produce a uniform coating film over the surface of the immersed crystal. The dissolving of the small proportion of salt by the enveloping film of water is strictly analogous to the alloying action which occurs during the hot-dipping coating process and makes this process a successful one for coating metals. Alloying of iron with molten zinc or tin is generally regarded by the men engaged in the zinc or tin coating industry as a more or less unavoidable nuisance incidental to the process. It is not generally recognized that, fundamentally, success in this process is attained almost entirely because of this behavior of the two metals.

In most cases of the commercial coating of metals by hot-dipping, the coating metal, zinc, tin, or aluminum, for example, alloys very readily with the "base metal," that is, the metal to be coated, for example, iron. In case the coating and base metals do not alloy directly, the same end may often be accomplished by the use of a small amount of a metal which does alloy with both of the others. This is usually done by making a suitable addition to the molten metal bath, though the same result may be attained if the "addition" is made as a surface film on the base metal before immersion in the molten metal. As will be explained later, although there is no mutual alloying whatsoever between the metals lead and iron, lead coatings on iron and steel are often secured by this means.

Although hot-dipping is essentially a method depending upon surface alloying, it should not be inferred that no coating whatever can be obtained if alloying between coating and base is lacking. Just as a film is produced over the surface of a clean glass rod when immersed in water, so also, if a clean metal surface, for example, iron, is brought into contact with a clean molten metal with which it does not alloy, lead for instance, a continuous coating film of the latter can often be made to cover the surface. The difficulties in producing such a continuous coating under these conditions are so great, however, as to render the process impracticable. Much of the difficulty arises as a result of the tendency of the coating during its solidification to coalesce more or less into globules, thus giving rise to breaks in the coating. This tendency is counteracted by the alloying action between the coating metal and the base.

The necessity for some alloying action between coating and base metals, in the hot-dipping coating process, is two-fold, therefore, although the second may perhaps be considered as a corollary of the other. First, slight alloying of the two insures a complete initial "wetting" of the surface of the base metal and therefore a uniform spreading of the molten metal over the surface; and secondly, as a result of this, the adhering film of metal solidifies without exhibiting any pronounced tendency to draw away from the base.

General Nature of Hot-Dipped Coatings

In no case is a metal coating which is produced by the hot-dipping process a simple film of the pure coating metal. As an unavoidable consequence of the necessary mutual alloying action, the coating must always be contaminated more or less with traces of the base metal, and its structure and properties must be somewhat different from those of a similar layer of the pure metal.

In structure a hot-dipped coating always shows evidence of at least two more or less distinct layers, the inner one being usually referred to as the "alloy layer." The metals used for coatings in the hot-dipping process are decidedly different in most of their properties from the base metals which are to be coated. The alloys formed by the union of unlike metals are usually not of a simple type, such as simple solid solutions or plain eutectic series, but of the more complex types in which intermetallic compounds occur. The inner or alloy layer of a hot-dipped coating is practically always made up in large measure of an intermetallic compound of the two constituent metals. Consequently this part of the coating is harder and more brittle than the outer layer which consists largely of the pure coating metal.

When a metal of high melting point, such as iron, is immersed in a molten metal of low melting point with which it alloys, such as zinc or tin, traces of it dissolve in the melted metal in the same way that salt dissolves in water. At the same time the molten metal combines with and diffuses to some extent into the solid metal, giving rise to a definite alloy layer. If the process is allowed to continue the diffusion may extend inward far enough so that a second layer forms, which is different from the first in its composition and properties. It is a singular fact that the alloy layers formed in this manner do not gradually merge, one into the other, but each is of a quite definite composition, and the change from one layer to the next is a decidedly abrupt one. When the immersed specimen with its outer alloyed surface is removed from the metal bath, it carries with it a surface layer of molten metal which by solidifying forms the outer layer of the final coating.

The relative thickness of the alloy layer in any hot-dipped metal coating varies with the kind of coating. For example, in a tin coating on iron this layer is very thin, whereas in a zinc coating on iron the alloy layer may under some conditions constitute the greater part of the coating. Since the amount of alloying in any case depends also upon the time, the temperature, and the mass of the parts, all these factors must be carefully regulated in practice. Prolonged immersion in the molten metal results in the formation of a thick alloy layer which renders the coating so brittle that for many purposes it may be useless.

Practical Aspects of the Hot-Dipping Process

In the simplest applications of the hot-dipping process, very little equipment besides handling tools and a container for the molten metal is required. For the coating of vast quantities of sheet and wire, however, which is done almost exclusively by this process, very elaborate mechanical devices have been developed. These are referred to briefly in later chapters.

Hot-dipped coatings are almost always relatively thick as compared with most other types of metallic coatings. In many respects, however, the hot-dipping process is somewhat wasteful of metal since there is no way of controlling accurately the amount of coating metal used and its distribution over the surface. In the case of materials of regular shape, such as sheet and wire, the uniformity of the coating can be fairly well regulated mechanically and the excess metal wiped off. With small pieces—nails, bolts, screws, and the like—a hot centrifuging is used to advantage in regulating the amount of coating metal left on; but for the great majority of pieces there is no simple and sure method for regulating both the amount of metal used and its distribution as a coating over the surface.

The hot-dipping process is a commercial success only with metals of relatively low melting point. For zinc and tin coatings and for some of the lead alloy coatings, its use forms the basis of one of the leading industries. Of the other metals of lower melting point, aluminum (m. p. 658.7° C., 1218° F.) is the only one which is used, and this only to a very limited extent. The production of cadmium coatings (m. p. 320.9° C., 609° F.) by hot dipping has not been seriously considered on account of the limited production of this metal. The difficulties involved in handling molten metals of high melting point, such as copper, nickel, or cobalt, in the large amounts necessary for the process have not encouraged experiments in the application of coatings of these metals by this process. The detrimental effect of the high temperature involved, if such coating metals were used, upon the properties of the metals to be coated is also a factor which is not encouraging.

Extension of the Hot-Dipping Process

If, instead of totally immersing the article to be coated in molten metal, a small amount of the coating metal is melted on the surface to be covered and then rubbed thoroughly over the surface, a coating can be produced which, in its essential respects, is the same as a hot-dipped coating. The tinning of copper sheets and containers is usually done in this manner. A slightly modified process consists in applying the coating metal as a powder, either dry or mixed into the form of a paste with a substance which serves the double purpose of binder and flux. When heated, the paste melts and under the influence of the flux spreads as a thin film over the surface. Lead, tin and zinc, as well as mixtures of the three metals, and silver appear to be the most suitable materials for this application. The process is of very limited commercial importance in the coating of metals although it is coming to be used as a means of repairing damaged coatings, particularly zinc coatings on steel structures or other large surfaces.

CEMENTATION

The characteristic feature of cementation, like that of hot dipping, is an appreciable alloying action of the surface layer of the treated metal.

Unlike hot-dipping, it does not necessitate the use of molten metal but consists in heating the metal while surrounded by another metal or non-metal, generally in a powdered form, to a temperature somewhat below the melting point of the more fusible of the two.

The process is of rather wide metallurgical application and was well known in ancient times. Copper, for example, was converted into brass by heating it in certain "favorable earths." Steel was made by heating iron in contact with charcoal. The latter process suitably controlled is, of course, the basis of the modern operation of "case hardening." By heating a soft, ductile (low-carbon) steel to a temperature of 870-900° C. (1600°-1650° F.) while it is surrounded by a carbonaceous packing material, the metal at the surface is converted to a considerable depth into a high-carbon steel by combining chemically with carbon which diffuses into it in the form of a gaseous compound. In the carburization of small parts in large volume the process may be carried out directly in gases, usually mixtures of carbon monoxide and hydrocarbons. Analogous to the carburization of steel is the nitrogen case-hardening process in which the surfaces of steel parts are hardened by heating to 925-1000° C. (1700-1830° F.) in a nitrogenous medium, usually ammonia gas. Nascent nitrogen liberated by decomposition of nitrogen compounds reacts readily with aluminum, chromium, vanadium, titanium, tungsten, manganese, molybdenum, etc., which may be present in the steel, forming dispersed nitrides and thereby surface-hardening the materials. Still another cementation process of surface hardening of steel consists in immersion in molten sodium cyanide at 850-870° C. (1560-1600° F.) The hardening produced by this treatment is more superficial than that obtainable in carburizing and nitriding and is due to the penetration of both carbon and nitrogen. These alloyed surfaces on steel are designed primarily, of course, for resistance to wear, although nitriding appears to be of some value in the prevention of corrosion.[2] The principle of cementation is, however, of considerable importance in producing coatings for the protection of metals against corrosion, and it is with this aspect that the present book is concerned.

Mechanism of the Process

It has long been known that certain metals diffuse into certain other metals merely upon contact at temperatures below their melting points.[3] Faraday and Stodart in 1820[4] observed that platinum alloys with iron upon the annealing at low temperatures of mixed powders of the metals. In 1868 Tohernoff showed that when two pieces of steel of similar nature are heated to about 900° C. in intimate contact they cohere. Experiments by Spring in 1882 indicated that alloying of metals may take place at ordinary temperatures merely by compression of the constituent metals, but Masing[5] several years later found that the function of pressure in this case was merely that of bringing the metals into more intimate contact. It was shown[6] in 1894 that very considerable alloying by cementation results if the ends of two carefully surfaced cylinders of a metal are pressed together for several hours at temperatures of from 200° to 400° C. That zinc readily alloys with an iron surface at relatively low temperatures was discovered accidentally in 1900 when zinc dust was used in the annealing of some iron and steel samples.[7] In recent years cementation coatings on iron have been produced with a great variety of metals and in some cases more than 1500° C. below their melting points.

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[2] Homerberg, V. O., and Walsted. J. P., *Trans. Am. Soc. Steel Treat.*, **16**, Suppl. 67 (1929); Malcolm, V. T., *Trans. Am. Soc. Steel Treat..* **16**, Suppl. 205 (1929); Sergeson, R., and Deal, H. J., *Trans. Am. Soc. Steel Treat.*, **18**, 474 (1930).

[3] For review and discussion of the subject of diffusion in solid metals see: Mehl, R. F., *Trans. Am. Inst. Mining Met. Eng.*, **122**, 11 (1936); Krynitsky, A. I., *Met. and Alloys*, **8**, 138, 173 (1937).

[4] Faraday, M., and Stodart, J., *Quart. Jour. Sci.*, **9**, 319 (1820).

It is evident from these observations that metals may interpenetrate merely upon intimate contact. In most cases the cementing metal has an appreciable vapor pressure at the temperature employed in the coating process and it is likely that at least some of the metal transferred to the surface of the base metal passes through the vapor phase. Both factors, contact of the metals and the presence of metal vapor, undoubtedly contribute to building up the coating as the process is carried out commercially. It is well known in zinc cementation that the intimate contact secured by "tumbling" the article being heated within the packing of zinc powder is necessary to secure uniform coatings. The presence of oxide films on the surface of a metal may retard or prevent cementation.

The penetration of the cementing metal into the surface of the base metal may occur in one or more of the following ways depending upon the nature of the metals involved, the temperature, duration of exposure, physical state of the base metal, orientation and size of crystals, pressure and character of contact: (1) by transfer through a solid solution, (2) by formation of an intermetallic compound, and (3) by migration along crystal boundaries.

Character of the Coating

A coating produced by cementation is simply a surface alloy layer of the base and coating metals. In most essential respects, it is comparable to the inner or alloy layer of a hot-dipped coating of the same metal. The coating metal, as such, does not enter into the structure of the coating except as particles may be mechanically entrained perhaps as a result of partial fusion resulting from too high an operating temperature.

It is characteristic of the process of cementation, at least for those metals which are capable of forming definite compounds with each other, that the alloy layer produced is not one in which the composition changes gradually from that of the "cementing" metal on the outside to that of the base metal on the inside. On the contrary, the coating is composed of sharply defined layers each of which is quite homogeneous, at least in its visible structure. Copper cemented with zinc dust forms an excellent demonstration of the structure of such coatings, on account of the difference in color of the different layers which form.[8] The outer silvery gray layer is much higher in zinc than is the inner one, which is a brilliant golden yellow, adjacent to the copper base. The relative thickness of the layers which make up the coating, and hence the average zinc content of the coating, is determined largely by the cementation temperature.

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[5] Masing, G., *Zt. anorg. Allgem. Chem.*, 62, 265 (1909).

[6] Spring, W., *Zt. Phys. Chem.*, 15, 65 (1894).

[7] Cowper-Coles, S., *Engg.*, 118, 277 (1924).

Alloy coatings are considerably harder and more brittle, as a rule, than those of the pure metal, and the chemical resistance is not the same as is that of the pure metal. In any comparison of the relative merits of coatings of the same metal made by different processes, for example, zinc coatings made by cementation and by electroplating, it should be borne in mind that metallurgically the two are of entirely different natures.

Practical Applications

The commercial production of protective coatings by cementation has been limited, until recently at least, to "sherardizing" by zinc powder, "calorizing" by aluminum powder and "chromizing" by means of chromium powder. Cementation by cadmium has been carried out successfully.[9] It has been shown [10] that in a similar fashion cementation coatings on steel may be produced at temperatures of 900° to 1200° C. with tungsten, vanadium, cobalt, uranium, titanium, silicon, zirconium, molybdenum, tantalum, boron, manganese [11] and beryllium.[12] Cementation with silicon was described more than twenty years ago [13] and has continued to interest investigators, the most recent development being the production of coatings by a process known as "Ihrigizing".[14] Many of these coatings display marked resistance to corrosion and it seems likely that they will come to be used on a commercial scale for the protection of ferrous metals. Although these cementation processes are used almost exclusively in the production of coatings on iron and steel, their application to other metals is apparent.

The cementation process, although particularly well adapted for small pieces, cannot very well be carried out on a small scale. The pieces are packed in the cementing metal powder in rather large containers which can be made fairly gas-tight and can be rotated about one axis so as to tumble the cementing powder over the surfaces to be coated. The whole must be heated for several hours and this is done by gas or by means of electric heating coils in the walls of the container. In some cases, as in calorizing, the process must be carried out in the absence of air, usually in an atmosphere of hydrogen.

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[8] Storey, O. W., *Met. Chem. Eng.*, 14, 683 (1916).

[9] Laissus, J., *Métaux*, 9, 537 (1934).

[10] Laissus, J., *Chim. Ind.*, 29, 515 (1933).

[11] Tsutomu Kase, (Abst.) *Metals and Alloys*, 7, 454 (1936).

[12] Laissus, J., *Rev. Métall*, 32, 293, 351, 401 (1935).

[13] Vawter, W. E., *J. Ind. Eng. Chem.*, 9, 580 (1917); Haslam, R. T., and Carlsmith, L. E., *J. Ind. Eng. Chem.*, 16, 1110 (1924); Guillet, L., *Compt. rend.*, 182, 1588 (1926).

[14] Anon., *Mach.*, 42, 540 (1936); *Ind. Bull.* (Arthur D. Little Co.) No. 112, p. 2, May, 1936.

Cemented or Sintered Carbide Coatings

Somewhat related to coating by cementation is the process of attaching sintered carbides to steel surfaces. The principal use of such coatings is for the production of cutting and grinding tools, although several localized wear and corrosion resistant applications have been suggested.[15] Carbides of tungsten, tantalum, titanium, etc. are prepared by heating intimate mixtures of the respective metal or oxide together with lampblack in a suitable atmosphere to temperatures ranging from 1500°-2400° C. The carbide thus formed is mixed with cobalt or nickel in the form of powder and heated until sintering. The carbides in a metallic binder of this kind, fashioned in suitable forms and shapes, are then brazed onto steel surfaces using copper, bronze or silver solders with suitable fluxes as the brazing media.

MECHANICALLY FORMED COATINGS: "METAL-CLADDING"

The veneering of base metal plate with noble metals has long been practiced, as previously mentioned. Just as the old process of making Sheffield plate depended upon the simultaneous rolling of silver and a copper-rich alloy, so also is the jeweller's gold-filled ware a gold or gold alloy shell filled with a base metal produced in a similar fashion. The commercial production of bi-metal strip, sheet or bars employing two base metals is of more recent origin. If a duplex ingot is made of two metals, that is, the central portion of one metal surrounded by a thick layer of the other, such as an iron or low-carbon steel center and copper covering, it is possible to roll the duplex ingot into the form of coated plate, bar or sheet; coated wire may also be drawn from the duplex billet. The finished product, in the example cited, has a coating of copper intimately alloyed to the steel base, the thickness of the coating being governed by the relative amounts of copper and steel in the ingot used and the amount of reduction received in working. Obviously the process is applicable only for those metals that do not differ radically in their rolling characteristics. The oxide film on alloy steels renders them difficult to bond to other metals by heating. In order to use them as a veneer for ordinary steel, their surfaces are electrolytically pickled in hydrochloric acid and electroplated with iron.[16]

Aluminum alloys are coated with commercially pure aluminum by casting an ingot of the alloy in a steel mold lined with sheet aluminum.[17] The aluminum coated aluminum alloy ingot thus produced is rolled to the desired dimensions without loss of continuity of the coating.

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[15] For details of process and bibliography see MacKenzie, "Metals Handbook," Amer. Soc. Metals, 772, 1936.

[16] Grimshaw, L. C., *Trans. Am. Soc. Mining Eng.*, 120, 363 (1936).

[17] Dix, E. H, U. S. Patent 1,865,089 (June 28, 1932).

It is reported that sheet zinc is successfully coated with aluminum by rolling sheets of zinc containing small amounts of aluminum together with aluminum sheets under pressure while hot.[18]

ELECTROPLATING

Electroplating is the most important method for the commercial production of protective metallic coatings with the possible exception of hot-dipping in the application of zinc and tin. Even in the case of zinc coatings recent advances have been mainly in the field of electrodeposition. Since the advent of chromium plating a few years ago there have been a number of new electroplating developments of promise such as heavy zinc coatings applied to wire, zinc, copper, nickel, and tin; brass coatings applied to steel strip; zinc and nickel coatings of markedly improved appearance; the electrodeposition of various alloys of controlled composition, etc.

Principles

The fundamental principles of the process of electroplating are familiar.[19] After a careful cleaning, the article to be plated is made the cathode of an electrolytic cell, *i.e.,* the plating bath, which is composed of a solution of the salt of the metal, the coating of which it is desired to electrodeposit. The anode of this cell is usually the metal which it is desired to electrodeposit but it may be another metal or some highly conducting material such as graphite which is insoluble in the plating bath under the conditions of operation. The plating operation is accomplished by passing a current through this cell, the source of electromotive force being a storage battery, a direct current generator or a rectified alternating current. Under the driving force of this applied potential, metal ions enter the solution by dissolution of the anode, and these ions and identical metal ions of the electrolyte move toward and reach the cathode and are there deposited in the metallic state. If the anode is of the insoluble type mentioned above the electrochemcial reaction at this electrode consists in the discharge of negative ions or anions and usually in oxygen evolution. In this case the metal ion content of the bath must be maintained by periodic additions of metal as oxide or hydroxide, thereby neutralizing at the same time the increasing acidity accompanying electrolysis under the circumstances.

According to Faraday's law the quantity of all of the elements liberated at either the anode or cathode during electrolysis is proportional to the quantity of electricity which passes through the solution. Since at the cathode hydrogen ions as well as metal ions may be discharged, the efficiency of the process of metal deposition may be, and usually is, less than 100 per cent. Similarly the dissolution efficiency of the anode may vary from the theoretical maximum to zero depending upon the proportion of the total current entering the solution by dissolution of metal. In certain plating baths anodes may undergo corrosion of the local action type, in which case the apparent anode efficiency may exceed 100 per cent. With any given plating conditions, the thickness of the deposit is proportional to the period of deposition.

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[18] Kesper, J. F., *Tech. Bläl, deut. Bergwerkzeit,* 23, 343 (1933).

[19] For a more complete discussion of the subject consult a text such as Blum and Hogaboom, "Principles of Electroplating and Electroforming," 2nd ed., New York, McGraw-Hill Book Co., 1930.

The successful operation of a plating bath requires the control of at least three variables, namely chemical composition of the plating solution, temperature of solution, and cathodic current density. These variables are related in their effect upon the character of the electrodeposit in such a way that if the range of one is changed it may be necessary to alter the others. Since it is usually desirable in commercial production to employ maximum current densities it is customary to adjust the bath composition, the temperature and other factors affecting the plating operation in such a way as to attain this end. Movement of the article being plated or movement of the plating solution with respect to this article generally permits the use of higher current densities.

Character of the Deposit

In actual practice, electroplating metal surfaces is not nearly as simple as might be inferred from the description given above. The character of the deposit, and hence its usefulness as a metallic coating, varies within very wide limits according to the plating conditions. First of all, the surface to be plated must be free from extraneous materials of all kinds. It is usually desirable that the deposited metal be distributed uniformly over the surface to be covered even though this surface be very irregular, as is often the case. In order to accomplish this purpose, solutions of rather complex composition are often employed. For example, alkaline cyanide solutions are particularly effective in depositing the required thicknesses of metal in recessed areas, thus exhibiting what is known as high "throwing-power." The use in certain baths of "addition agents" which often are of a colloidal nature is another method of obtaining this result. The deposits obtained by both of these means are usually smooth and fine grained in character. In the first case the fine grain structure results from the small, but constant, concentration of metal ions provided by dissociation of complex cyanide ions, while in the second case the restricted grain-size is due to the polarizing effect of the addition agent.

The deposition of coatings of uniform thickness is dependent also upon the proper arrangement and spacing of the parts to be plated with respect to the position of the anodes. The movement of the cathodes in the solution, as in "barrel" plating, aids in uniform distribution of deposited metal over the surface. Owing to the irregular shapes of many articles certain areas are generally nearer than other areas to the anodes and for this reason receive somewhat heavier deposits.

The importance of porosity of coatings depends upon the electrochemical relation of the coating metal to the base metal; if it is electronegative or anodic toward the base metal in the environment in which the article is to be used the existence of pores in the coating is not particularly disadvantageous, since under these circumstances the coating metal protects the underlying metal by sacrificing itself. If, on the other hand, the coating metal is electropositive or cathodic to the base, corrosion of the base metals will occur—the well recognized "pinhole" rusting. To illustrate, where iron is to be protected, coatings of zinc or cadmium may contain pores without seriously reducing their protective value, whereas if the coatings are of such metals as copper or nickel, continuity and freedom from pores are essential to prevent corrosion.

The formation of pores or pits in electrodeposits is generally associated with the adherence to the cathode surface either of gas bubbles, usually hydrogen, or of suspended particles of a miscellaneous character. The presence of metallic impurities of low hydrogen overvoltage in the base surface is conducive to hydrogen bubble formation, particularly in baths of high acidity.

It is essential that the metal be deposited in a dense, compact condition. Porous spongy deposits may occur owing to the formation of metal hydroxides and their codeposition with the metal. This is particularly true of relatively neutral solutions in which the film of solution adjacent to the cathode readily becomes alkaline as the evolution of hydrogen proceeds. If the solution is a dilute one and unagitated, so that the solution film adjacent to the cathode surface is depleted of metal ions, this tendency toward a spongy deposit is also pronounced.

The adhesion of electrodeposited coatings to the base metal depends primarily upon their intimate contact. The presence of grease, oxides or other extraneous materials markedly reduces adhesion. It is well known that a roughened surface, such as produced by sandblasting, improves the bond between coating and base probably by a mechanical keying action. Under suitable conditions the crystals of the deposited layer may be formed as direct extensions of the crystals in the base metal.[20] Such a coating becomes an integral part of the article. While instances of incipient diffusion of copper and gold coatings into zinc at ordinary temperatures have been observed, it may be said that, in general, electrodeposits do not alloy with the base metal unless subsequently heated.

METAL SPRAYING AND SPRAYED METAL COATINGS

Production of metallic coatings by spraying has attained commercial importance in the protection of metals from corrosion. Any metal available in the form of wire and fusible in the oxyhydrogen flame can now be sprayed on almost any surface. While the process is particularly suitable for the application of coatings to large structures, such as storage tanks and bridges, it is also used in the coating of small articles. In repair shops metal spraying is now commonly employed to build up worn or undersized parts. This application, as well as such miscellaneous uses as the metallization of non-metallic surfaces, is outside the scope of the present book.

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[20] Blum, W., and Rawdon, H. S., *Trans. Am. Electrochem. Soc.*, **44**, 305 (1923); Graham, A. K., *Trans. Am. Electrochem. Soc.*, **44**, 427 (1923).

The metal-spraying process is associated with the name of the Swiss engineer, M. U. Schoop, who more than anyone else is responsible for its sucessful commercial development. The process is a special application of an older process of powdering metals. In 1882 a process of making lead powder by passing a stream of molten lead through a gaseous blast was patented in Germany. Somewhat later, mechanical methods of atomizing metals were developed in Switzerland and France. In principle these methods consisted in allowing molten metal to impinge upon rotating paddle-wheels. Schoop conceived the idea of preparing a metal coating by placing the article to be coated directly in the path of the atomized metal.[21] In experiments with lead bullets fired against a stone wall Schoop had observed that the flattened masses adhered to the wall and that upon overlapping the bullets appeared to be welded together. As early as 1902 a process for producing a metal coating by impacting metal dust upon a base by means of a blast of unheated gas was patented but never used commercially. Some years later Schoop devised a successful modification of this process by providing for the use of ignited gas.[22] It was the design of a nozzle permitting an annular blast which had encouraged the first commercial development of the metal-spraying process by Schoop and his associates about 1910. At this stage a stream of molten metal supplied from a reservoir was employed. This reservoir of molten metal with the auxiliary parts weighed over a ton and the dust-spraying apparatus weighed over a hundred pounds—serious handicaps to the commercial utilization of the process.

The use of metal in the form of wire for spraying had been proposed in 1905. Some years later a suitable apparatus known as a "pistol" was designed for this application.[23] Subsequent developments of spraying equipment have all utilized some form of portable pistol whether for powder, wire, or liquid metal. The modern wire pistol weighs between three and four pounds. In the operation of this, and of the powder pistol as well, melting of the metal is accomplished by the use of an oxyhydrogen or oxyacetylene flame. The electric arc has been utilized as the source of heat in some designs thus making the apparatus still more portable.[24]

Typical gas-fired pistols in common use are those shown in Figure 8. In such instruments the metal in the form of wire is advanced into the nozzle of the pistol at a constant rate such that the end of the wire is melted and atomized continuously. The size of wire used depends upon the metal to be sprayed, and the character of the deposit desired. In general, wires 0.125 inch in diameter may be used for heavy-duty spraying, while for ordinary deposits, wires from 0.08 to 0.03 inch in diameter (approximately

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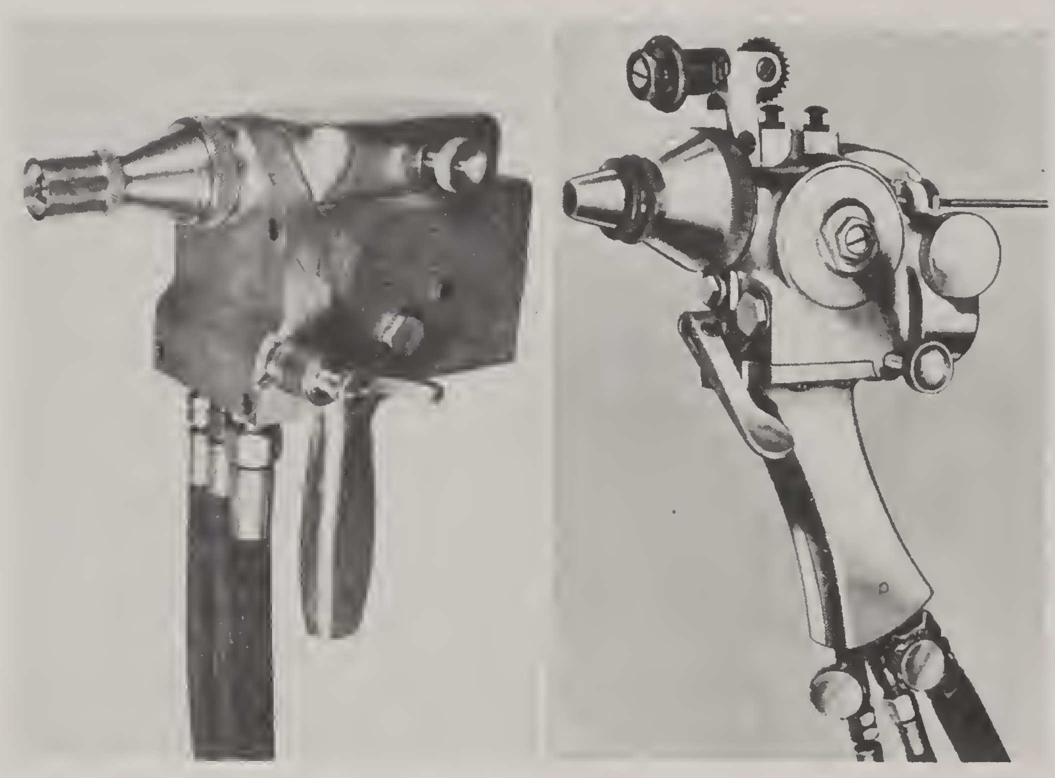
[21] Turner and Budgen, "Metal Spraying," p. 5, London, Chas. Griffen & Company, 1926.

[22] Schoop, M. U., U. S. Patent 1,128,059 (1915).

[23] Morf, U. S. Patent 1,100,602 (1914).

[24] Kasperowicz, W., *Zt. angew. Chem.*, **31 I**, 144 (1918); Gerber, F., *Die Metallbörse*, **23**, 510 (1933).

12 to 21 Brown and Sharpe gauge) are commonly used. The higher-melting metals spray more readily in the smaller wire sizes. These smaller sizes are used also where fine texture of deposit is desirable.



Courtesy of Metals Coating Co. of America, Metalspray Co., Inc.

Figure 8.—American Types of Gas-fired Metal Spray Pistols.

In its simplest form, the nozzle of the gas-fired pistol consists of three concentric tubes as shown diagrammatically in Figure 9. The wire to be sprayed is advanced through the central one; through the annular space surrounding this central tube, the gaseous mixture of either hydrogen or acetylene and oxygen is passed, which upon burning at the orifice melts the wire in the inner part of the conical flame. Through the second or outer annular spaces passes the compressed air or other gas which accomplishes the atomizing and spraying of the metal as it is melted. Acetylene and oxygen are used at pressures of 15 pounds per square inch and air at 50 to 60 pounds per square inch. From the standpoint of the energy consumed the process is inefficient, about 2 to 3 per cent of the heat of the flame being utilized in melting the metal.

The driving mechanism for feeding the wire is usually a small air turbine driven in some designs by the compressed air used for spraying the metal. Among other mechanical features which are of interest are modifications or extensions of the nozzle, and rotating nozzles to permit spraying inside of pipes or other rather inaccessible surfaces. (Gas jets may be attached to the pistol when it is desirable to heat the surface being sprayed.)

The electrically operated pistol differs considerably in construction and operation. Two wires are used which for a portion of their length conduct the current, and upon arcing at the ends produce the heat necessary for melting the metal. It is possible with this pistol to spray the higher-melting metals such as molybdenum and tungsten.

The powder process of metal spraying is limited commercially to metals of low melting point and in particular to zinc which can be obtained reasonably cheap in the form of powder as a by-product from zinc smelters. The pistol invented by Schori[25] for the powder process consists essentially of two injector arrangements, one a blow pipe and the other an aspirator. The finely divided metal is sucked from the powder chamber by the aspirator and heated as it passes through the flame of the blow pipe. The coating produced is essentially the same in character as that produced by the wire-pistol process.

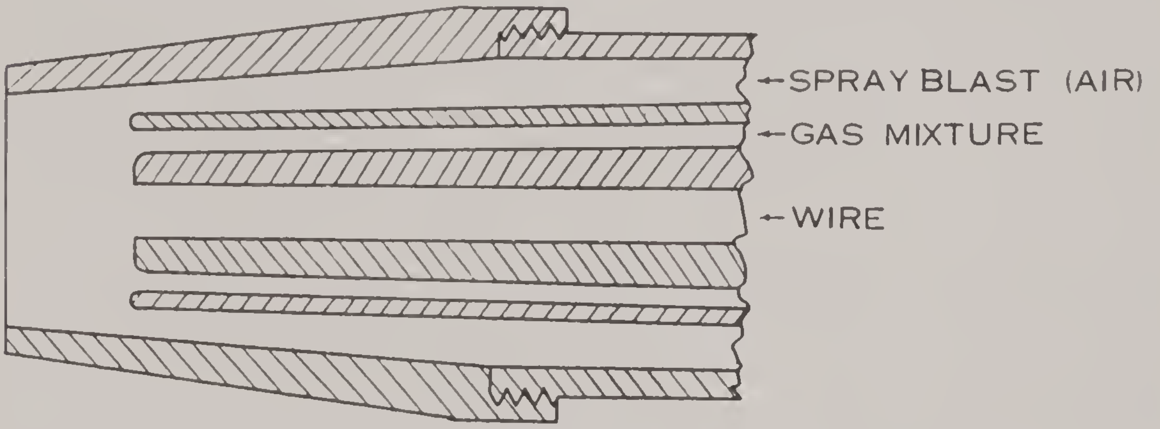


Figure 9.—Essential Features of the Nozzle of a Metal Spraying Pistol in which a Gas Flame is Used for Melting the Metal Wire.

In a later modification of the process of using liquid metal a pistol was developed by Jung in Holland to accommodate four pounds of metal previously melted in a gas-heated crucible. This process also is limited to low-melting metals, and the pistol is rather heavy. It is said to be rapid in operation and to produce coatings of uniform character.[26]

For coating small parts tumbling or revolving barrel machines have been devised, mainly abroad. Usually the articles to be sprayed are preheated in a separate compartment. The spray-guns are so arranged at the ends of the drum that the work is in the range of the spray during the tumbling operation. It requires from 10 to 20 minutes under these conditions to coat articles with zinc depending upon the thickness of coating desired.

The efficiency of deposition of sprayed metal coatings depends upon the process employed, the metal used and the distance of the nozzle from the surface being sprayed. For the wire pistol with the nozzle from 4 to 8 inches away the efficiencies of deposition are claimed to be as follows: Aluminum, 90-85% ; high-carbon steel, 85-75% ; brass, 80-75 % ; zinc and tin, 73 to 67% ; and lead, 65-60%.[27]

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[25] British Patent 432,831.

[26] Lippert, T. W., *Iron Age*, 134, 8, Aug. 30 (1934).

Surface Preparation for Metal-Spraying

The most common method of preparing a surface for metal-spraying is that of sandblasting. Steel grit and cracked shot may be used instead of sand, and pickling in 4-per cent sulfuric acid is used to a limited extent where small articles are to be coated. It is desirable to apply spray coatings within a few hours after sandblasting in order to avoid superficial oxidation or contamination of the surface.

The adherence of sprayed coatings to the base is largely of a physical character, and depends upon roughening of the base surface. The sandblasting operation produces angular indentations and recesses which provide an improved anchorage for the coating. In contrast to electroplated coatings, which may under certain conditions continue the microstructure of the base metal, sprayed coatings are not so firmly bonded to the base metal. The strength of the bond in the latter case, however, is adequate for most practical purposes and has been shown to be as high as 700 pounds per square inch for coatings sprayed on properly sanded surfaces.[28]

The Nature of Sprayed-Metal Coatings

The fact that fine fabrics and other combustible materials may be metal-sprayed is astonishing at first acquaintance. If, however, a thermometer is placed in the range of the spray at a distance of 4 or 5 inches from the nozzle of the pistol it will be found that the temperature is but approximately 70° C. Evidently the metal in the wire process is melted, sprayed and again solidified at least superficially all in a small fraction of a second. Very likely the air film adhering to the surface of objects such as fabrics insulates them against heating until the deposited metal is cooled by the accompanying air blast. Schoop's original concept that fusion of the particles occurs at the instant of impact owing to the conversion of their kinetic energy into heat was later shown mathematically to be untenable.[29] A later microscopic study of metals sprayed upon glass indicated that the metal is either in a molten or plastic condition upon striking the surface to be sprayed and that a certain amount of spattering occurs upon impact. The powder process does not give the splash effect to such an extent as the wire process. Aluminum deposits made by this process have been found to consist almost entirely of rounded particles of metal each having a dendritic structure.[30]

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[27] Tech. Bull. 106, Nov. 15, 1936, issued by Metals Coating Company of America, Philadelphia, Pa.

[28] Kunkler, L. E., *Mech. Eng.*, 58, 639 (1936).

[29] Arnold, H., *Zt. angew. Chem.*, 130, I, 209, 218 (1917); *Met. Ind., (London)*, **12**, 121, 146, 165 (1917).

[30] Rollason, E. C., *J. Inst. Metals*, **60**, 35 (1937).

It may be concluded from these observations that the particles upon striking the surface are flattened into relatively thin scales thus increasing the "covering power" of the metal. It is well known that these particles suffer superficial oxidation during the operation of spraying, in which compressed air is used. The characteristic stratification or lamination of sprayed metal deposits is apparently an oxidation effect. The undulating contours shown in the microstructure of cross-sections of sprayed coatings reveal the manner in which the deposits are built up from the component flattened and superficially oxidized metal particles. In spite of the oxidation effect, sprayed coatings made by the wire-pistol process have a high intrinsic tenacity.

As stated in the previous section, there is ordinarily no alloying action between the metal of the coating and that of the base metal. Similarly it has been shown that in coatings produced by spraying successively two different metals, for example, zinc and copper, no evidence of alloying of the two to form brass could be detected in the microstructure.[29] On the other hand, using an electric spray gun with a copper and a zinc wire [31] or spraying copper and zinc simultaneously [32] it is possible to produce deposits containing a certain amount of brass.

The density of sprayed metal is less than that of the same metal in cast form. In Table 2 is given a comparison of the values of density obtained for sprayed metals with the accepted values for the same metals in the ordinary form.

Table 2.—Density of Sprayed Metals Compared with the Density of the Metals in the Ordinary Form.

	Density of Sprayed Metal		Density (Int. Crit. Tab.) of Ordinary Metal
	Turner and Ballard [34]	Arnold [29]	
Aluminum	2.4	2.31	2.70
Zinc	6.4	6.32	7.14
Tin	7.1	6.82	7.31
Iron	6.5	...	7.86
Copper	8.0	7.51	8.92
Lead	...	9.77	11.34
Brass	...	7.32	8.30*
Bronze	...	7.77	8.76*

* Cast form of same alloys used for sprayed metal by Arnold.

This difference in density is to be attributed in part to oxidation and in part to the presence of pores and cavities. In the case of copper it has been shown [33] that the oxygen content of the coating may run from 0.3 to 1.25 per cent depending upon the design of the pistol, the oxygen pressure and distance of the nozzle from the surface to be sprayed. Porosity tests made upon similar copper deposits by immersion in a non-reacting oil *in*

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[31] Schoop, M. U., and Kasperowicz, W., *Schweiz. Elektrotech. Zt.*, 16, 33 (1919).

[32] Experiment carried out at Nat. Bur. of Standards and referred to by H. S. Rawdon, "Protective Metallic Coatings," p. 48, Chemical Catalog Company (Reinhold Publishing Corp.), 1928.

[33] Ballard, W. E., and Harris, D. E. W., *Met. Ind. (London)*, 49, 482 (1936).

vacuo showed an absorption of oil comparable in its variation to the oxygen content. It is of interest to note that the porosity, as well as the oxygen content of the coating, may be reduced by using an inert gas instead of compressed air for spraying. By skillful manipulation of the air pressures in the ordinary method it has been found possible to spray coatings of lead, tin and zinc which are impervious to liquids.[34] Similar attempts to produce impervious coatings of copper, aluminum and brass were not successful.

The porosity of sprayed coatings may be reduced by mechanical treatment, as for example, hammering or wire brushing. Heating the article to be coated beforehand or spraying a thin coating of a low-melting metal, such as tin, and heating it to fusion before spraying the principal coating are other methods of overcoming porosity. Sprayed zinc coatings have the property of corroding in moist air to form corrosion products which fill the pores and improve the continuity of coating. The use of copal or Bakelite varnishes on sprayed nickel not only reduces the porosity of the coating, but appears to improve its adherence to the base metal.[35]

The particles of sprayed metals are, according to x-ray analysis, slightly work-hardened[36] and this together with the presence of oxide results in a hardness in excess of that of the same metal in the cast form. In Table 3 values are given for Brinell hardness of certain sprayed metals

Table 3.—Brinell Hardness Numbers of Deposits of Various Metals Made Under Different Conditions.

Metal or Alloy	Type of Pistol	Projecting Gas	Projecting Gas Pressure (kg/sq. cm.)	Distance Projected (cms.)	Brinell Hardness of Deposit	Brinell Hardness of Large Mass of Metal or Alloy
Zn	wire	air	4	18	23	24
Zn	wire	air	4	18	23.5	24
Zn	powder	air	4	18	17.5	24
Zn	wire	N	4	18	19.	24
Zn	wire	N	4	5	18	24
Al	wire	air	4	18	35	21
Al	wire	N	4	18	35	21
Al	wire	air	2.5	18	28	21
Al	wire	N	2.5	18	32	21
Al	wire	air	4	5	40	21
Al	wire	N	4	5	36	21
Al	wire	air	2.5	5	26	21
Al	wire	N	2.5	5	30.5	21
Al	wire	air	4	18	84.5	50
Al	wire	N	4	18	90	50
Al	Spl. powder	air	4	18	102	50
Brass 70/30	wire	air	4	18	103	58
	wire	N	4	18	58	58
Mild Steel	wire	air	4	18	199	118
	wire	N	4	18	168	118
Stainless Steel 18/8	wire	air	4	18	187	160
	wire	N	4	18	106	160

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[34] Turner, T. H., and Ballard, W. E., *J. Inst. Met.*, 32, 291 (1924).

[35] Reininger, H., *Trans. Faraday Soc.*, 31, 1268 (1935).

[36] Ballard, W. E., *Mech. World*, 97, 103 (1935).

obtained in a recent investigation.[37] The coatings were 2 to 3 millimeters in thickness and the measurements were made with a ball 1.98 millimeters in diameter. The values given are the average result of three experiments.

In general, it will be seen that the sprayed metal is harder than the same metal in the ordinary form. It would appear from an inspection of these results that the deposits made with the nitrogen blast are lower in hardness than those in which the projecting gas is air.

The effectiveness of various sprayed metals in the protection of iron, steel and certain non-ferrous alloys against corrosion will be discussed in later chapters. It may be mentioned here that as compared with electroplated and hot-dipped coatings relatively greater thicknesses of sprayed metals are required to give the same measure of protection. For example, it is common practice for the protection of ferrous metals to use sprayed zinc and aluminum coatings 0.004 to 0.010 inch in thickness, depending upon the severity of the exposure. Similarly, tin and lead coatings run 0.010 to 0.020 inch in thickness and nickel coatings somewhat higher. In a comparison of the relative qualities of coatings sprayed by the wire and powder processes there was little difference observable for zinc (although the test had not been completed) but aluminum deposited by the wire method appeared to be superior.[30]

Practical Applications of Metal Spraying

Unlike most other types of metal coating, metal spraying may be readily applied to large and extensive metal surfaces *in situ*. Moreover the thickness of the coating can be controlled within rather narrow limits, and its composition can be varied. The coatings may be of commercially pure metals or of alloys such as Monel metal or brass, or they may be of two or more metals successively applied.

The foregoing features have led to the application of sprayed coatings to bridges, gas tanks, electrical transmission towers, hulls of ships, dock gates, the framework of street cars, tank cars, etc.

The small-scale applications of metal spraying are exceedingly varied and numerous, and no attempt will be made to list all of them. Certain structural parts of refrigerators, washing machines, furnace grates, condenser pipes, baffle plates, staybolts, screws and so on, have been successfully metal sprayed.

The use of metal spraying as a supplement to other coating processes is of interest. Sherardized coatings not infrequently show spots where the coating is either very thin or is lacking entirely. Such areas can be easily and quickly covered by metal spraying and rejections because of imperfect coatings can be almost entirely eliminated.

CATHODE SPUTTERING

When a relatively high voltage is applied between two electrodes in a partial vacuum inducing a glow discharge, it is found that the cathode undergoes disintegration and that the metal thus removed is deposited as a thin film on nearby objects within the tube. With a suitable design of tube or chamber it is possible so to arrange objects with respect to the cathode that their surfaces will be more or less uniformly metallized. This process, known as cathode sputtering, consists of three phases, namely, generation of metal gas, diffusion of gas, and condensation of gas in the form of a metal film.

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[37] Fassbinder, J., and Soulary, P., *Met. Ind. (London)*, 49, 35 (1936).

It is well known[38] that the cathode metal is vaporized by local heating induced by positive ion bombardment. The potential required varies from 500 to 2000 volts depending upon the nature of the cathode metal. The greater part of the vapor thus produced condenses on the cathode itself, but a fraction of it diffuses throughout the tube and deposits as a sputtered film. The diffusion process is, of course, much influenced by the conditions of the vacuum, that is, the pressure, temperature and the nature of the other components present. While at lower pressures (10^{-4} millimeter of mercury) the atoms are diffused in a straight line, at the pressures existing in the sputtering chamber, 0.01 to 0.1 millimeter of mercury, the ordinary laws of diffusion prevail, with the result already described. The emitting cathode remains relatively cold during the process of sputtering as do other objects in the chamber on which the vapor condenses. Owing to this fact, it is possible to metallize paper, fabrics, waxes, etc., by this process.

The residual non-metallic gases in the sputtering chamber may influence the sputtering of certain metals. To avoid chemical reactions inert gases or hydrogen are generally employed. The rate of metal deposition is increased by sputtering in a heavy gas, being about fivefold more rapid in argon than in hydrogen.[39]

The metallic sublimate or deposit obtained in sputtering is crystalline in character and of a very fine-grained structure. It is assumed[40] that the metal is deposited in an amorphous state and that it subsequently crystallizes. There is evidence that the rate of crystallization is restrained by gases occluded in the deposit.[41] It is of interest that an increase in porosity of the film appears to be associated with crystallization. While thin films of sputtered metals may be highly porous, it is possible by increasing the thickness to about 0.001 millimeter to obtain deposits which are substantially pore-free.

Equipment and Methods of Operation

A sputtering chamber consists essentially in a vacuum-tight vessel fitted with a small anode, a large cathode and a fixture near the cathode for holding the object to be sputtered. The chamber is readily constructed from a bell jar fitted upon a heavy ground-glass plate. In certain commercial uses vacuum chambers of capacities up to six cubic meters are employed.[42] The anode may be located at a somewhat remote point in the chamber or even outside the chamber proper in a tube sealed into the vacuum line. It is customary to produce the necessary vacuum with a large capacity pump connected to the bell jar through a short length of large tubing. The vacuum system contains a McLeod gauge for reading pressures, and a bleeder valve. A constant pressure of residual gas may be maintained by operating the pump continuously and allowing air or inert gases to leak in slowly through the bleeder valve. Another method of operation consists in the use of a pressure regulating device which will stop and start the pump as required. It usually requires from 5 to 10 minutes to reduce the pressure of the system to the range 0.01 to 0.1 millimeter of mercury required for sputtering. The power may be satisfactorily supplied by means of a transformer which steps up the voltage from 110 to 10,000 volts using a rheostat in the primary winding for regulating the current.[43]

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[38] Hippel, A. v., *Ann. Physik*, 81, 1043 (1926).

[39] Cartwright, C. H., *Rev. Sci. Instruments*, 1, 758 (1930).

[40] Reinders, W., and Hamburger, L., *Ann. Physik*, 10, 668 (1931).

[41] Joliot, F., *Ann. Physik*, 15, 437 (1931).

Commercial Applications of Sputtered Coatings

There are certain special applications in which cathode sputtering may be advantageously used for the production of metallic coatings. The process is particularly suitable for the metallization of electrically nonconducting materials, such as fabrics and phonographic recording waxes. The deposition of small amounts of silver in surgical gauzes by this means is said to provide materials of high oligodynamic action for the treatment of wounds.[44] In the metallization of sound recording waxes it is essential that the microscopic details of the surface receive a smooth continuous and adherent coating. This is faithfully accomplished by cathode sputtering with the production of a surface of improved quality for sound reproduction.[42]

Cathode sputtering has been successfully used in gold coating thin aluminum alloy diaphragms for carbon broadcasting transmitters.[43] It is necessary in this application that the gold coating be adherent, continuous and free from contaminating substances such as plating salts. Deposits of gold 0.001 millimeter in thickness produced by this method have proved superior in quality to electroplated gold coatings for this use. The aluminum alloy surface is suitably prepared for sputtering by scratch-brushing followed by rinsing first in acetone, then in ether, and finally by rubbing dry with filter paper.

COATINGS BY CONDENSATION OF METAL VAPOR

Closely related to cathode sputtering, but of more recent origin in practical application, is the production of metallic coatings by the condensation of metal vapors produced by thermal rather than electrical means. In this case the material to be evaporated is brought in contact with a heating coil or placed in a small electrically heated magnesia, alumina or graphite crucible which in turn is fitted into a coiled filament.[45] Tungsten and platinum wires are suitable for the heating elements. It is necessary to employ a higher vacuum in this process than in cathode sputtering. Pressures of 10^{-4} millimeter of mercury are satisfactory and must be maintained during the operation.

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[42] Richter, K., *Koll. Zt.*, 61, 208 (1932).
[43] Fruth, H. F., *Physics*, 2, 280 (1932).
[44] Fischer, German patent application.

Metal deposition by this process is more rapid than by sputtering and it is possible to exercise better control of thickness. The temperature of the system must be maintained within certain limits. Should it become too high, the deposit becomes non-adherent and pulverulent owing to the fact that the metal gas density becomes so great as to cause condensation in the vapor phase.[42]

The following metals have been deposited by the thermal evaporation method: aluminum, antimony, beryllium, bismuth, calcium, chromium, cobalt, copper, gold, iron, lead, magnesium, manganese, nickel, selenium, silver, tellurium, tin and zinc. The method is generally not suitable for the deposition of alloys since there is a tendency in this case for the components to be fractionally distilled. While this process of producing metal coatings cannot be said to have attained commercial importance as yet, it shows considerable promise of special applications in the future.

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[45] Cartwright, C. H., and Strong, J., *Rev. Sci. Instruments,* 2, 189 (1931).

Chapter 4

Zinc Coating by the Hot-Dipping Process

The largest single use of zinc is in the form of zinc coatings. In 1934 over 42 per cent of the metallic zinc consumed in the United States was used for this purpose. This does not include the amount of this metal used as zinc dust, zinc oxide, lithopone and other zinc pigments in protective paint coatings. It is safe to say that fully half of the entire production of zinc is used for protecting other metals, notably iron and steel, against corrosion. The term "galvanized" as applied to zinc-coated iron had its origin in the concept of the "galvanic" (electrochemical) protection from corrosion afforded iron by contact with zinc.

It was in 1786 that Luigi Galvani, an Italian physiologist, described his classic observation that the suspension of frogs on an iron railing by copper hooks caused twitching in the muscles of their legs when the legs touched the railing—a reaction caused, as Volta later recognized, by the electric current generated by contact of dissimilar metals. "Galvanic action" thus came to arouse considerable interest and seems to have been recognized as a factor in the resistance of zinc-coated iron to corrosion.

Having been used since the early part of the 19th century the term "galvanized iron" has become rather firmly fixed commercially. In this book the word "galvanize" will be restricted to the process by which a zinc coating is produced by immersion in molten zinc, a process which might well be referred to as "zinc-dipping" in order to distinguish it from the other zinc-coating methods. The term "zinc-coated" will be used as descriptive of all articles coated with zinc irrespective of the process by which the coating may be applied.

History of Zinc and the Hot-Dipping Process

It seems unlikely that the ancients had any acquaintance with zinc although a bracelet of silver inlaid with zinc has been reported from the ruins of Camiros which was destroyed in 500 B.C. Brass, however, was known in Biblical times. About 300 B.C. the Mossynoeci made brass by melting with copper a peculiar earth known as *calmia* which was found near the shores of the Black Sea.[1] The alchemists, notably Albertus Magnus, who lived in the 13th century, were familiar with the existence of zinc minerals which could be used to impart a golden color to copper. Zinc was not definitely recognized as a metal until Ebener in 1509 separated it from zinc slag or furnace calamine. Paracelsus (1493-1541) first referred to the metal using the term *Zinken.* The production of zinc by distillation from calamine was carried out by Kenkel in 1741 and by von Swab in 1742 and the production of the metal on a commercial scale was undertaken at Bristol in 1743.[2] There is considerable evidence that zinc was known and produced in the East long before it was in Europe. It is recorded that in 1745 an Englishman went to China to learn the process of zinç smelting. The Dutch in 1640 captured a Portugese ship laden with a cargo of zinc secured in the East.[3] The name "spailter" or "spiauter" used for the cargo is suggestive of the commercial term "spelter" still widely used for cast slab zinc.

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[1] Rickard, T. A., *J. Inst. Metals*, 43, 297 (1930).

The first recorded experiments for producing zinc coatings by the dipping method are those of a French chemist, Melouin, in 1741. Tinned iron was already known at that time and Melouin attempted to zinc-coat iron sheets in a similar manner by immersion in a bath of molten zinc. The results of his experiments formed the basis of a report to the Académie Royale in 1742. Jean-Baptiste Kemerlin attempted to apply this process to coating kitchen utensils and the like in 1742, and by 1778 the use of zinc-coated iron utensils seems to have been fairly well known in parts of France.

In the description of the process given by Bishop Watson (*Chemical Essays,* 1786), sal ammoniac (ammonium chloride) was said to have been used.[4] There is evidence, however, that Bauschaendorf of Leipzig brought about the change from the use of a resinous flux to that of ammonium chloride. Bauschaendorf also recommended the use of a preliminary tin coating before immersion in the molten zinc, a practice which, although very early discarded, still survives in the usual dictionary definition of the process.

Sorel in 1836 was granted a French patent for a zinc-coating process which had practically all the essentials of the process as it is known today. The articles were to be cleaned in dilute sulfuric acid (9 per cent by volume), washed in water for 12 or 14 hours, then put in dilute hydrochloric acid and, after drying, immersed in a bath of molten zinc which was kept covered with a layer of ammonium chloride. On being removed from the zinc bath the articles were to be well shaken to remove excess metal and then plunged into cold water, after which they might be rubbed with sand and dried. The Sorel process was investigated by the French naval authorities and a very favorable report rendered concerning the protection from corrosion rendered to iron by this treatment. At nearly the same time, 1837, an English patent was granted to H. W. Crawford for a very similar zinc-coating process by hot-dipping which made use of ammonium chloride as a flux. A previous English patent granted in 1805 to Hobson, Sylvester, and Morehouse, which covered a method for coating iron with sheet zinc for the purpose of corrosion protection, may be cited as illustrating the importance attached to zinc as a protective metallic coating. The commercial development of the zinc-coating industry in England and in the United States is generally conceded to be the outgrowth of Crawford's patent rather than of Sorel's.

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[2] Sang, A., *Rev. Métal.,* 9, 1, 78, 160, 275, 343 (1912). This reference contains a rather complete historical development of the zinc coating process, and has been used freely in preparing the present account.

[3] Moulden, J. C., *J. Roy. Soc. Arts,* 64, 495, 517 (1916).

[4] Trewin, C. S., *Bull. Am. Zinc Inst.,* 8, 43, May (1925).

Coating wire with zinc was one of the first large-scale commercial applications of the zinc-coating process carried out mechanically. The coating of sheets was done entirely by hand in the early days of the industry. The patent of Morewood and Rogers in 1846 marks the first advance in the sheet-coating industry, in that mechanical regulation of the thickness and uniformity of the coating by means of rolls was attempted. They also recommended the use of an initial coating of tin to precede the zinc coating, as had Bauschaendorf previously. Experience showed, however, that the use of a preliminary tin layer was of no advantage and in fact was detrimental; therefore, it was gradually discontinued.

The success attained with the use of the coating machine for tin-plate, about 1863, stimulated action in the zinc-coating industry but, primarily on account of the very much larger sheets which had to be handled, it was not until a number of years later that a real solution of the problem was attained.

Outline of the Hot-Dipping Process

The hot-dipping process for covering metal products with metal coatings in theory is very simple. The article to be coated is properly cleaned and then completely immersed in the hot metal, and withdrawn with enough of the molten metal adhering as a surface film to give it the desired coat. In practice the process is not so simple, even with hand dipping. Preliminary cleaning of the metal products to be coated, fluxing of the surface of the bath of molten metal, regulation of the bath temperature and the use of addition agents in the metal are important factors, each of which has a bearing on the quality of the coating produced.

The dipping process as practiced for the production of zinc coatings is entirely manual for irregularly shaped articles such as structural parts, castings, bolts, nuts, nails and similar hardware, and such fabricated articles as ash cans, laundry tubs, vats, tanks and pails. Pipes are also, for the most part, dipped by hand. The dipping of materials of regular shape, *e.g.*, sheets, wire, woven wire fencing, etc., is done by means of machines, and involves larger tonnages than the hand-dipping process.

Preparation of the Base Surface

Cleaning the surface of the materials before coating is an essential operation, since the quality of the coating is markedly influenced by the character of this surface and its freedom from extraneous substances. There are two steps in the process of surface preparation following degreasing: the first consists of a pickling treatment in acid in which the oxide scale and inert material are removed from the metal; the second is a fluxing treatment, applied prior to submersion in the molten zinc bath, which serves to remove traces of oxides or iron salts. The iron surface prepared in this fashion is wettable by molten zinc. The same general method of surface preparation differing somewhat in details is used for wire, pipe, and other steel and iron products.

Pickling Treatment for Removal of Scale

The pickling bath used for removal of the scale layer from iron and steel is usually dilute sulfuric acid, although dilute hydrochloric acid is coming to be used more widely [5] and phosphoric acid to some extent for this purpose.[6]

In cleaning sheet stock the black sheets, suitably spaced in a basket of some alloy resistant to the action of the acid, such as aluminum bronze, are treated with dilute acid in a wooden tank or a steel tank lined with a rubber coating. The solution is kept warm either by coils of a lead pipe through which steam is passed or by jets of steam in the solution. The rate of pickling in sulfuric acid depends mainly upon the temperature of the bath and to a less extent upon the concentration of the acid. The best practice is to use from 4- to 8-per cent acid at a temperature not to exceed 80° C.[7] The average pickling conditions for sheets consist in the use of 7-per cent sulfuric acid at 60 to 95° C. and the time required under these conditions is 15 to 20 minutes.[8] When hydrochloric acid is used for pickling the rate of scale removal depends mainly upon acid concentration, and the operation is carried out at temperatures not exceeding 40° C. and usually in the range of 20 to 30° C. where the rate of pickling is comparable to that obtained with sulfuric acid under the average conditions given above. For cleaning castings, dilute hydrofluoric acid (approximately 5-per cent) is often used initially in order to dissolve grains of sand adhering to the surface. A surging of the solution up and down between the sheets is necessary as a mechanical aid in removal of the scale as it becomes loosened during the pickling operation. This is often accomplished by moving the sheets up and down in the solution. It is now known that the pickling acid loosens the scale by dissolving the underlying ferrous oxide layer of the scale which exists at the metal-metal oxide interface in the case of scales formed at higher temperatures.[9] It is of interest that scales formed at lower temperatures (below 575° C.) which should not contain appreciable amounts of ferrous oxide require longer periods for pickling. The mechanism of the acid attack on scale appears to be electrolytic in nature: the acid reaches the iron surface through pores in the scale and forms thereby electrolytic cells in which iron dissolves anodically and the scale (principally magnetic oxide with an outer skin of ferric oxide) being cathodic, is reduced to ferrous oxide which in turn is soluble in the acid.[10] The mean loss in weight resulting from the removal of the oxide scale from sheets is 150-300 grams per double-sided square meter of surface.[11]

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[5] Bablik, H., *Iron Age*, 123, 879 (1929).

[6] Hudson, J. C., *(Discussion) J. Iron Steel Inst.*, **126**, No. 2, 187 (1932).

[7] Imhoff, W. G., *Iron Age*, **126**, 82 (1930).

[8] Camp, J. M., and Francis, C. B., "The Making, Shaping and Treating of Steel," 4th ed., pp. 903, 968, Pittsburgh, Pa., Carnegie Steel Company (1925).

[9] Winterbottom, A. B., and Reed, J. P., *J. Iron Steel Inst.*, **126**, No. 2, 159 (1932).

It has become customary to use inhibitors in the pickling of iron in order to minimize the attack of the acid upon the metal surface. The development and general adoption of the modern inhibitor, together with improved pickling operations, have resulted in an overall reduction in acid consumption of 30-40 per cent.[12] Among substances which have been used more or less effectively as inhibitors in pickling baths are glue, gelatin, quinoline, pyridine, diethylamine, thiourea, sulfonated oils, etc. The use of such restrainers appears to be more necessary in sulfuric acid than in hydrochloric acid, where the rate of attack on the metal is low, particularly when it is used cold.[13] In the preparation of sheets for hot-dipping the use of minimum percentages of inhibitors has been found to prevent excessive liberation of hydrogen, which is sometimes conducive to blistering, without interfering with the slight roughening of the surface which is essential to the satisfactory adherence of the coating.[14]

It may be observed that these organic inhibitors are positively charged colloids or organic compounds which ionize readily. These substances become adsorbed on the cathodic areas of the iron as the scale is removed and restrain the discharge of hydrogen.[15] The resulting retardation of the acid attack upon the iron has been discussed in Chapter 1 and attributed to cathodic polarization. There is evidence that the inhibitive efficiency of certain organic compounds depends upon the structure and stereochemical arrangement of their positive ions.[16]

The pickling of iron and steel by electrolytic methods has been practiced to some extent. It has long been common practice to clean small parts by making them cathodic in warm alkalies. The Bullard-Dunn cathodic descaling process [17] makes use of an acid sulfate bath containing a small proportion of a metal salt such as stannous sulfate. As the scale is removed a thin deposit of tin is progressively formed over the cleaned areas and inhibits the solution of iron. More recently it has been proposed to descale iron by anodic pickling in dilute sulfuric acid or acidified ferrous sulfate solution.[18]

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[10] Hoar, T. P., *(Discussion) J. Iron Steel Inst.*, 126, No. 2, 191 (1932).

[11] Bablik, H., "Galvanizing," 2nd ed., London, E. & F. N. Spon, Ltd. (1936).

[12] Russel, P. R., *Am. Zinc Inst.*, 18th Annual Meeting (1936).

[13] Swinden, T., and Stevenson, W. W., *Fourth Report of Corrosion Comm. of Iron and Steel Inst. and British Iron and Steel Federation*, p. 185, (1936).

[14] Munger, H. P., *Trans. Electrochem. Soc.*, 69, 85 (1936).

[15] Jimeno, E., Grifoll, I., and Morral, F. R., *Trans. Electrochem. Soc.*, 69, 105 (1936).

[16] Mann, C. A., *Trans. Electrochem. Soc.*, 69, 115 (1936).

[17] Fink, C. G., and Wilber, T. H., *Trans. Electrochem. Soc.*, 66, 381 (1934).

[18] Müller, R., and Harant, L., *Trans. Electrochem. Soc.*, 69, 145 (1936).

After sufficient pickling the sheets are washed with water, and are sometimes stored in a tank under water until ready to be coated. Immediately before coating the sheets are immersed for a few seconds in cold dilute (5- to 10-per cent) hydrochloric acid to remove the superficial rust which forms after pickling. In hand-dipping pieces of irregular shape the articles are thoroughly dried at this stage before being immersed in the metal bath. In the machine zinc-coating process some of the excess moisture is sometimes removed by rubber rolls before the sheets pass through the flux on their way to the molten zinc bath.

Fluxing Treatment

That portion of the surface of the metal bath through which the article is passed into the molten metal is kept covered with a flux which is commonly ammonium chloride, although zinc chloride or a mixture of the two may be used. There is, as a matter of fact, considerable variation both in the material used as the fluxing agent and in the manner in which it is applied. For example, a solution of ammonium chloride may be used together with hydrochloric acid, in place of hydrochloric acid alone, in the second stage of the pickling operation described in the last paragraph above. Another modification, the most modern practice, omits this step entirely and employs a solution of zinc and ammonium chlorides used in a ratio of one molecule of zinc chloride to three molecules of ammonium chloride.[19] Since the role of this bath is that of a deterrent to oxidation and a solvent for zinc oxide in or on the molten zinc, it is properly considered as a fluxing treatment. This solution containing from 5 to 20 per cent of the combined salts (depending upon the nature of the work to be fluxed) may be used either hot or cold.

The iron surface following the fluxing treatment is coated with a thin film containing ammonium chloride which, upon coming into contact with the molten zinc dissociates, yielding hydrochloric acid. This acid dissolves any oxide remaining on the iron surface and permits the zinc to wet the iron. It is of interest to mention that when an iron surface is cleaned by abrading with emery and then dipped in molten zinc no coating will form owing to the presence of an air-formed film of oxide.[20]

Other Methods of Surface Preparation

The oxide scale may be removed from iron by immersion in fused salts. Usually mixtures of sodium salts sometimes including caustic soda are used. It is claimed that a particularly effective means of cleaning telegraph wire consists in making the wire the cathode in a cell employing molten sodium hydroxide and sodium carbonate as the electrolyte.[21] Another pretreatment, an annealing step, sometimes used in the preparation of steel wire consists in passing it through molten lead prior to immersion in the zinc bath.[22]

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[19] Baldwin, A. T., *Steel*, 99, 49 (1936).
[20] Daniels, E. J., *J. Inst. Metals*, 49, 169 (1932).
[21] Tainton, U. C., *Wire and Wire Prod.*, 9, 399 (1934).

Very recently it has been proposed to pretreat steel strip stock before immersion in the molten zinc bath by first heating the material in an oxidizing atmosphere at a temperature in the range from 170 to 500° C. (338 to 932° F.) to form a uniform oxide coating (appearing as a yellow to gray film) and subsequently reducing this thin oxide by passing the strip heated to the normalizing temperature (935-950° C.) through a reducing atmosphere, cooled to about 150° C. (302° F.) Finally the steel strip is passed into the zinc bath while still protected by the reducing atmosphere.[23] It is claimed that the film of reduced iron produced on the steel surface by this treatment improves the adhesion of the zinc coating and reduces its tendency to flake or chip off upon deformation.

The Molten Metal Bath

The ordinary bath used for coating steel sheets contains approximately 30 tons of molten zinc,[4] and "pots" containing as much as 75 tons are not uncommon.[8] The container used is either of open-hearth iron or a low-carbon steel plate, either riveted or welded together. Cast containers are used only for very small jobs. A coke fire was formerly used almost exclusively as the source of heat, but coal or oil has now, to a large extent, replaced it as a solid fuel, and natural gas is used considerably in this country. In the large installations the heat is transferred to the metal bath through the sides of the container rather than through the bottom. An electric furnace of the resistance type with a capacity of 8 tons of zinc has been developed for the zinc coating of small castings, pipes, etc.[24] In coating sheets and wire the machines for guiding the steel stock through the metal bath are placed partly beneath the surface of the molten zinc.

In many instances, a layer of lead 6 to 8 inches or more deep is used in the bottom of the zinc bath. The two metals, zinc and lead, are miscible only to a very slight extent. The main purpose served by the lead layer is to prevent overheating of the lower walls of the container, particularly when the pot is first started, and to reduce the attack of the zinc upon the hot walls of the container, thus adding to its life and also cutting down the amount of zinc-iron alloy, or dross, formed. It also serves as a cushion upon which the dross floats, which aids materially when the dross is removed. If lead is not added as such to the molten zinc, it is practically always present in appreciable quantity in the slab zinc used so that a lead layer gradually forms in the bottom of the pot.

Formation of Iron-Zinc Alloy or Dross

Upon immersion in molten zinc, a steel or iron article to be coated attains the temperature of the molten bath and is dissolved at its surface by the zinc. This alloying action between the two metals is an essential feature in the coating of metals by hot dipping. As will be shown later, the coating produced is far from being a simple layer of zinc but is rather complex and consists essentially of two rather sharply defined layers. The inner or alloy layer has a higher fusion point than the outer one, which is essentially zinc. The properties of the coating are very materially affected by this structural condition.

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[22] Schueler, J. L., *Agr. Eng.*, 14, 339 (1933).
[23] Sendzimir, T., U. S. Patent 2,110,893 (March 15, 1938).
[24] Owen, S. Z., (Westinghouse Elec. Mfg. Co.) *Elec. J.*, 28, 631 (1931).

Naturally the walls of the container as well as all iron and steel parts immersed in the zinc bath are subject to attack by the molten zinc, so that the bath soon becomes saturated with iron. However, the principal source of iron in the zinc bath is from the decomposition of iron salts which may be carried over in the form of superficial films from the pickling or fluxing operations.[20] At 450° C. the saturation point or limit of solubility of iron in molten zinc is approximately 0.10 per cent of iron.[25] As the amount of iron in the zinc bath is increased beyond the solubility limit, crystals of the iron-zinc alloy, represented approximately by the formula $FeZn_7$ (10.9 per cent Fe), crystallize out of the molten metal and, being of slightly greater density than the zinc, slowly settle to the bottom of the zinc and float on the molten lead. The alloy-rich layer which forms is termed "dross."

The accumulation of the dross gradually interferes with the operation of the bath so that it has to be removed periodically, usually once a week. The material removed consists of a zinc-rich matrix, embedded in which are the crystals of the iron-zinc compound. The average iron content of the dross of "hard zinc" as it is often called is very considerably below that of the compound $FeZn_7$, since this compound in contact with zinc absorbs zinc without loss of its crystalline character until it becomes a solid solution. Analyses of plant dross generally show from 2 to 3 per cent iron.

The resistance of steel to the alloying action of molten zinc is but little affected by carbon contents up to 0.3 per cent; but above this and notably around 0.5 per cent carbon, the attack is markedly increased. Similarly the presence of 0.2 per cent silicon in iron results in a three-fold increase in rate of attack by molten zinc, whereas from 0.03 to 0.37 per cent manganese, 0.08 per cent sulfur, or 0.055 per cent phosphorus have practically no influence.[26] A phosphorus content of this order is considered by some to improve coating adherence.

The alloying action of molten zinc on iron is accentuated by an increase in temperature, particularly in the range above 500° C. Below this temperature it has been shown that the following relationship holds for the solvent action of high purity zinc on mild steel:[27]

$$L = n\sqrt{t}$$

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[25] Peirce, W. M., *Trans. Am. Inst., Mining Met. Engrs.*, **68**, 767 (1923).

[26] Musatti, I., and La Falce, A., *Met. Ital.*, 28, 1 (1936).

[27] Daniels, E. J., *J. Inst. Metals*, **46**, 81 (1931).

where L is loss in weight of a unit area, n is a constant at a constant temperature, and t is time of immersion. Above 500° C. the relationship becomes

$$L = Nt$$

where N is a constant at a constant temperature and L and t have the same meaning as given above.

Thus it would appear that below 500° C. the rate of attack is determined by the rate of diffusion of zinc through a compact superficial layer of $FeZn_7$, but that above this temperature the alloy layer becomes porous and presents no impediment to attack. There is evidence that the change in character of the alloy layer occurs between 480 and 500° C. It is considered that a kettle should have a life of from 10 to 18 months if given proper care.[8] Calculations employing the equations given above indicate the following values for the life of a kettle with a wall thickness of 1.5 inches if used at the temperatures given:

At 432° C. (810° F.)—2410 years
477° C. (890° F.)—1487 years
500° C. (932° F.)— 28 days
540° C. (1004° F.)— 19.6 days

The average working temperature usually regarded as suitable in coating sheets is 450° C. and for zinc coating of wire from 445-465° C.[28] For large heavy objects in which the surface area is relatively small as compared to the mass of the body, bath temperatures as low as 425° C. are recommended in contrast to temperatures of 475° C. which might be suitable for small parts.[29] Since it is necessary in any case that the articles attain the temperature of the bath in order that adherent coatings may form, large pieces must remain in the zinc considerably longer than small ones. The tendency is for increased alloying action in the coatings as the period of immersion is increased, the temperature remaining constant, hence the reason for a somewhat lower coating temperature recommended for the heavier pieces.

At the exit end of the metal bath, a flux covering is not used, except in some very special cases. In the hand-dipping process, the surface is cleaned off with a wooden spatula just before the article is brought out. At the most, only very slight oxidation occurs which has no effect upon the weathering properties of the coating although it may alter the appearance somewhat. After hand-dipping, the coated article, such as a tub, is turned upside down to allow all excess zinc to drain off and may also be rapped sharply to aid in removing the excess zinc. Machines have been devised for removing the excess zinc from small articles, bolts, nuts, nails, small castings and the like by shaking or centrifuging, or by a combination of the two.

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[28] Finkeldey, W. H., *(Discussion) Am. Electrochem. Soc.*, 47, 201 (1925).
[29] Touceda, E., *Foundry*, 42, 470 (1914).

Most zinc-coated wire, except that known as telegraph wire, is "wiped" as it emerges from the molten zinc to remove excess zinc and to give a smooth surface. The wiper may be a pad of asbestos which can be held on the opposite sides of the wire by suitable adjustable steel clamps. Telegraph wire is not wiped and hence has a somewhat rougher appearance than fence wire. In the latter case if the wiping is very severe only a very thin coating remains, which may consist almost entirely of the zinc-iron alloy layer. This is shown in Figure 10 which also shows the effect of bending upon coatings of this kind. The wiping of wires during galvanizing is not simply for the purpose of saving zinc, as is often supposed, but is often necessary to produce a coating which will withstand rather severe bending.

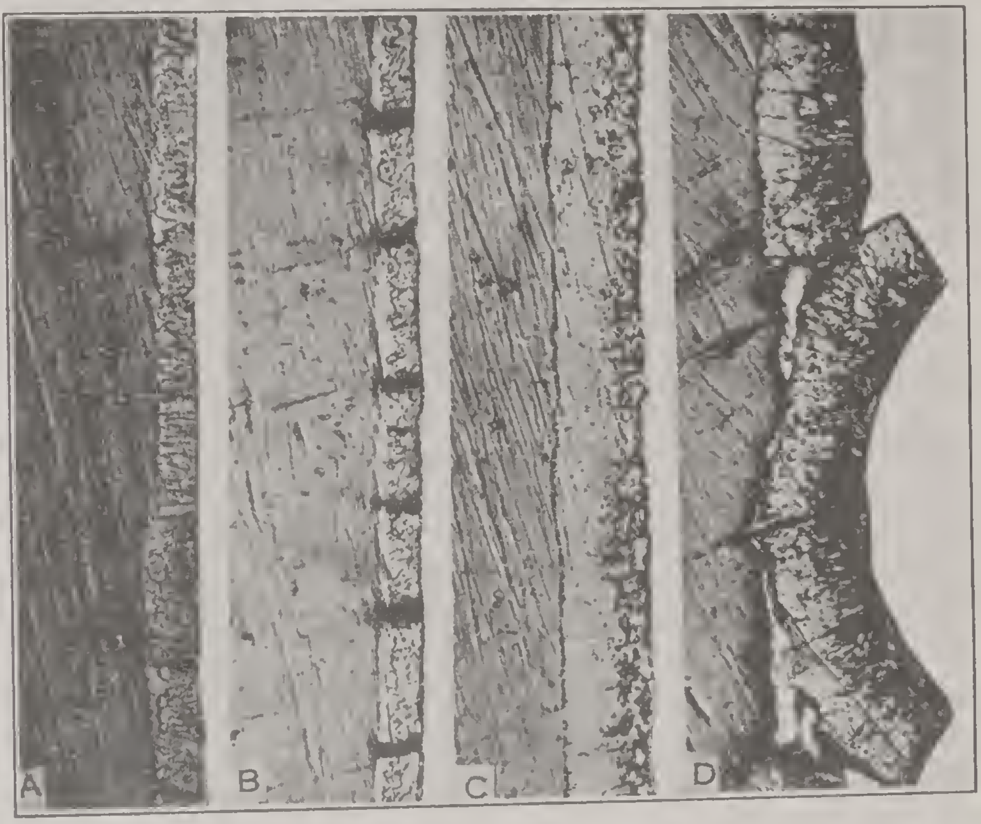

Figure 10.—Structure of Zinc Coating on "Wiped" Wire. ×350[30]

A. Tight Wiped Wire. All the coating except the alloy layer has been wiped off.
B. Same as "A" after the bend test in which it was wrapped around a wire of the same diameter.
C. "Asbestos-Wiped" Wire. This coating was not so closely wiped as in "A."
D. Same as "C" after the bend test of "B." The rough uneven surface of the alloy layer is largely responsible for the flaking upon bending.

For making wire with exceptionally heavy coating, the wiping may be done by drawing the wire vertically from the bath through a "header" of sand, charcoal or fine cinders. A hollow cone of zinc quickly freezes around the wire and functions as a wiper.

In coating sheets by machinery, the thickness of the coating can be regulated, at least approximately, by setting the exit rolls with respect to the surface of the zinc bath. By slightly changing the position of the rolls (often by adding more zinc to the bath), so as to increase the amount of zinc in the V-groove between the two rolls, a thicker coating is obtained, other conditions in operation remaining the same. The thickness of the coating on sheets varies somewhat from sheet to sheet and may vary rather widely on different portions of the same sheet. A variation of 17.5 per cent, that is, a variation of 0.35 ounce per square foot in a nominal coating of 2 ounces per square foot, is considered by many manufacturers [8] as good commercial practice even with present-day equipment.

Effect of Metallic Additions to Zinc Bath

It has been mentioned on a previous page that the presence of certain amounts of carbon and silicon in iron influences the rate at which it is attacked by molten zinc. In a similar way various metals when present in the zinc bath may affect both the rate of alloying with iron or steel and the character of the zinc coating so produced.

Aluminum.—The addition of 0.05 to 0.25 per cent aluminum (added in the form of a zinc-aluminum alloy) is widely used in the hand-dipping process for irregularly shaped articles. The greatly increased fluidity of the bath so produced is an advantage in affording greater penetration of the zinc into all crevices where in fabricated articles such as pails, dippers, tubs, etc., it must function as a solder as well as a protective coating. The use of aluminum is not generally favored in the coating of sheets in this country since it tends to produce dark spots on the surface. The presence of aluminum results in a decrease in the thickness of coating [11] and a marked reduction in thickness of the iron-zinc alloy layer [30] as shown in Figure 11. In appearance the coating assumes a relatively permanent bluish white lustre.

Tin.—It is customary to add tin to the zinc bath to improve the surface appearance and increase the uniformity and adherence of coating. While the use of tin in proportions as high as 3 per cent is reported, it is more common to employ less than 1 per cent. Tin produces large featherlike spangles white in color.[31] The effect of tin on the zinc-dipping process is, in all probability, to be ascribed to its influence on the melting point of zinc. The addition of even small percentages of tin causes the freezing of the metal to be spread over a considerable range of temperature, solidification not being complete until a temperature of 198° C. has been reached.

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[30] Finkeldey, W. H., *Proc. Am. Soc. Testing Materials*, 26, Part 2, 304 (1926).

[31] Brayton, G. A., *Address 18th Annual Meeting Am. Zinc. Inst.*, St. Louis, Mo., April 21, 1936.

Cadmium.—The presence of cadmium in excess of 0.05 per cent in the zinc bath increases its corrosive action toward iron and produces a coating of inferior bending qualities.[32] Cadmium does not of itself attack mild steel[33] but when present in the zinc bath it appears to render the $FeZn_7$ layer granular in character and thereby to obviate the restraining influence on the dissolution of iron otherwise exercised by the alloy layer.[20] Owing to this detrimental effect of cadmium it is desirable to avoid the use of cadmium-bearing zinc in the coating of telegraph and telephone wire, since such wire must be heavily coated and still be capable of withstanding severe deformation.[34] Very high-grade zinc has been used in coating the wire used in suspension bridges such as, for example, the Hudson river bridge at Bear Mountain, New York, and the Delaware river bridge at Philadelphia.[4] Cadmium is said to produce a silver fern-like spangle.

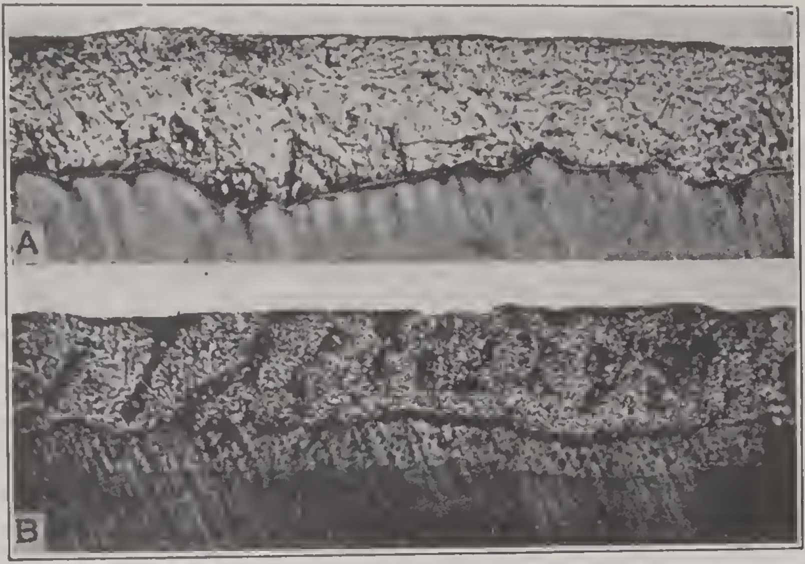

Figure 11.—Effect of Additions to Zinc Bath on Structure of Coatings. ×350[30]

A. The bath was treated with 0.2 per cent aluminum. Note the absence of alloy layers.

B. The bath was treated with tin. The oblique markings in the outer, or zinc-rich layer of the coating are the patches of tin-zinc eutectic.

Antimony.—The addition of antimony decreases the size of spangles in the coating even in the presence of considerable proportions of lead. In appearance the spangles assume a bluish lustre and have been described as "pearly"[35] and "ice-flowerlike."[36] Excessive percentages of antimony in the bath produce a yellowish stain in coatings.

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[32] Bablik, H., *Metal Ind. (London)*, **37**, 411 (1930).

[33] de Lattre, G., *Rev. Métal*, **25**, 630 (1928).

[34] Ingalls, W. R., *Metal Ind. (New York)*, **14**, 429 (1916); Stone, G. C., *Iron Age*, **98**, 86 (1916).

[35] Imhoff, W. G., *Metal Cleaning Finishing*, **8**, 143 (1936).

[36] Arndt, L., *Z. Ges. Giessereipraxis*, **52**, 395 (1931).

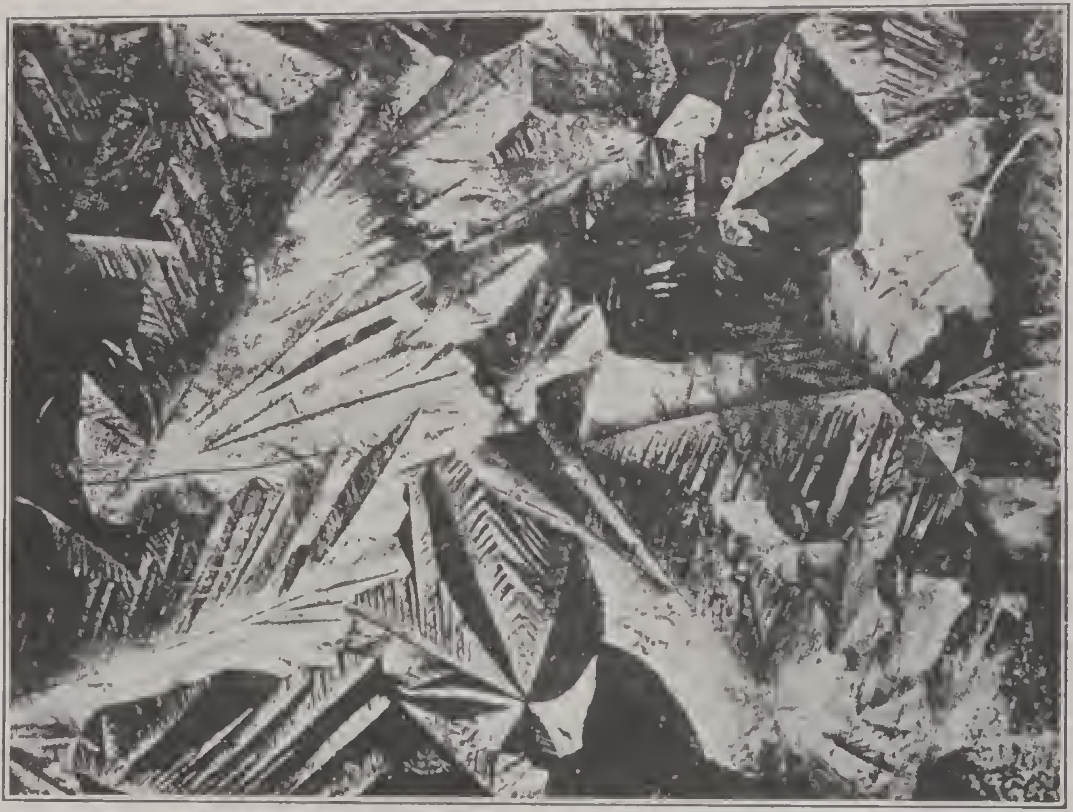

Figure 12.—Zinc-coated Sheet Showing Very Large "Spangles," Natural Size.[37]

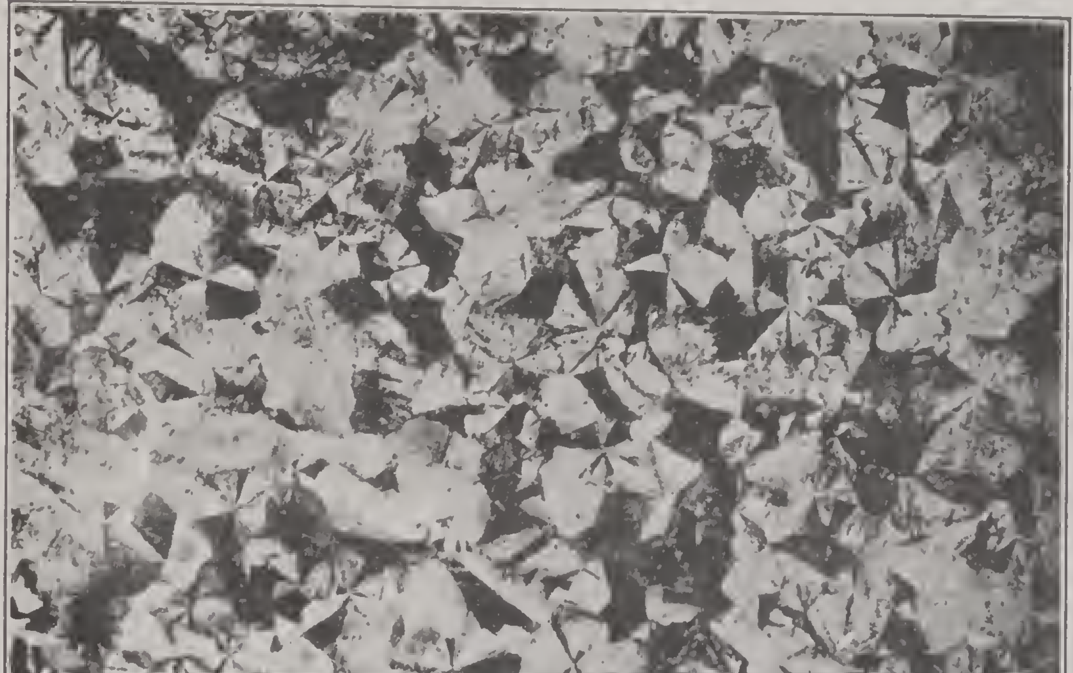

Figure 13.—Zinc-coated Sheet Showing Medium Size "Spangles," Natural Size.[37]

Other Factors which Affect Character of Zinc Coatings

The nature of the surface of the basis metal plays a part in determining the character and particularly the appearance of the zinc coating. The highest possible uniformity and cleanliness of sheet surface is essential for good coatings. Not infrequently the sheets after coating have a rough gray appearance, sometimes in certain portions only, and at other times over the entire surface. The beautiful fern-like pattern or spangle shown in Figures 12 and 13, which is regarded as desirable and is characteristic of high-grade material, may be entirely lacking on such sheets. This type of defect, the "gray sheet," illustrated in Figure 14, is often a cause of serious concern to sheet manufacturers. Although the character of the spangle is intimately related to the nature of the impurities in the zinc bath, as described in the preceding section, experience has shown that gray sheets may come from the same bath from which the majority of sheets coated at the same time are satisfactorily spangled. It is of interest that when representative gray sheets are stripped of their coatings by dilute acid and then passed through the galvanizing bath a second time, gray coatings are again obtained.[37] Similar results were obtained on sheets which were gray in certain restricted areas indicating that the location of the gray areas was

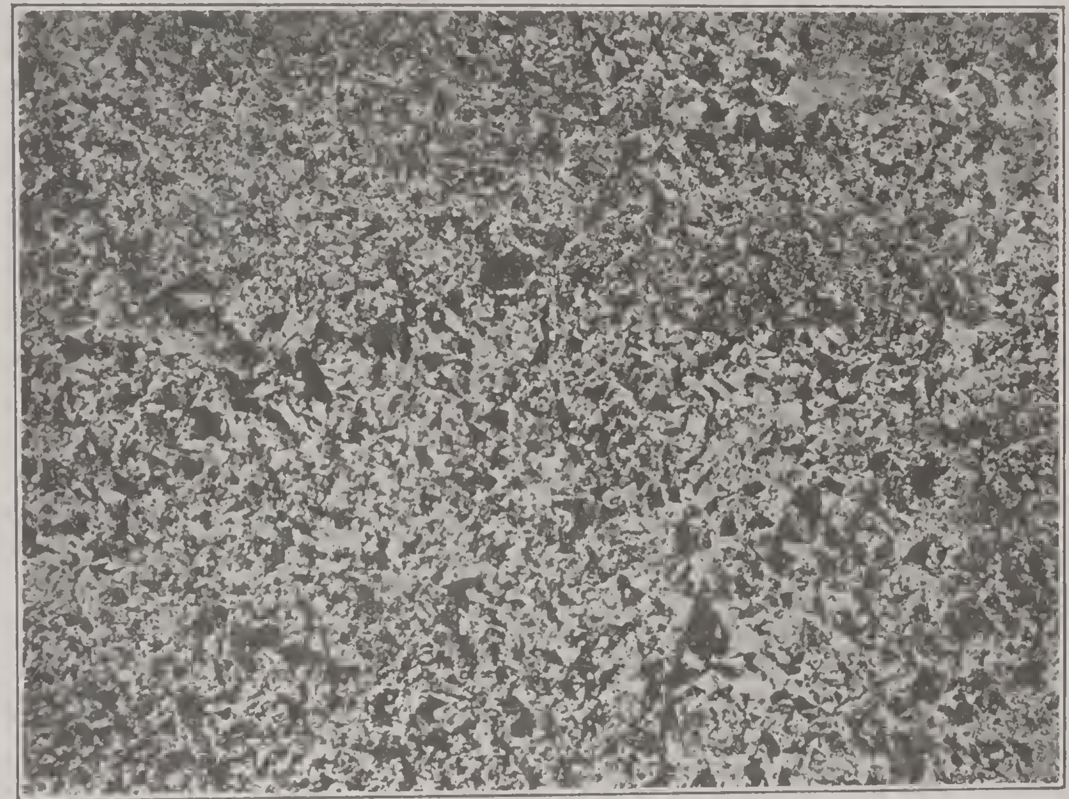

Figure 14.—Zinc-coated Sheet, Natural Size, Showing a Granular Dull Appearance Generally Known as "Gray Zinc."[37]

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[37] White, G. A., *Iron Age*, 101, 934 (1918).

permanent. Coated wrought-iron sheets never have the beautiful spangled surface shown by coated steel sheets, their characteristic appearance resembling more that of gray sheet. However, if a wrought-iron surface is cleaned mechanically, that is, without pickling in acid, a marked change results and the spangle is often well developed.

There is evidence that one factor in the production of gray sheets is the retention of hydrogen by the iron during pickling. The surface of gray sheets from which the zinc has been removed has been found to be covered with blisters [37] which it is assumed were caused by hydrogen evolution upon contact of the steel with molten zinc. These blisters would be expected to provide numerous crystallization centers giving rise to the characteristic small crystalline coating. The inferiority of coatings on steel having pearlite along the grain boundaries has been attributed to the escape of hydrogen which had previously penetrated into the discontinuities in the grain structure of this steel.[38] In general, it may be said that any condition favoring a large number of nuclei for crystallization is conducive to the gray appearance.

Blisters in galvanized sheets are practically always associated with defects of the steel base rather than with the coating. On the whole, however, blistering is not a very common defect in zinc-coated steel sheets.

Adhering spots of the black or dark-colored flux which are sometimes termed "sally spots" in the mill, constitute one type of defect occasionally experienced. These are primarily defects in appearance only as it can be shown by removing the adhering deposit that the sheet is coated with zinc underneath the spots. Such spots are generally scraped off and the sheets passed through the zinc bath again. Incomplete removal of the oxide scale in the pickling operation usually results in bare or "black spots." Many such sheets can be reclaimed by scraping the spots free from scale, cleaning them with acid and recoating the sheet in the zinc bath.

Examination of galvanized sheets which have been slightly weathered often reveals many features which to one experienced in the manufacture of such material tell much concerning the preparation of the sheets. Lightly coated sheets often show transverse dark bands or "chatter marks" after weathering. The dark bands are generally considered to be somewhat of the nature of ripples in the alloy layer, the formation of which was caused by the "chattering" of the machine. There is no evidence to indicate, however, that chatter marks are to be considered as serious defects.

Very heavy zinc coatings do not completely solidify for several seconds after the sheet leaves the bath. It sometimes happens that the coating flows slightly on the sheet and causes a roughened, rippled surface. Such coatings are often referred to as "slipped coatings."

The contact of the links of the chain used for conveying the sheet away from the pot as it emerges from the bath usually causes early freezing of the zinc coating at these contact points. Large, well-developed rosette crystals or spangles form around these spots and thus record the position of the conveyer chain on the sheet.

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[38] Schwarz, v., M., and Fromm, H., *Korrosion u. Metallschutz*, 11, 241 (1935).

THE MICROSTRUCTURE OF IRON-ZINC ALLOYS

The pronounced solvent attack of molten zinc on iron or steel in contact with it has been repeatedly referred to in the foregoing discussion of the process of zinc coating by hot dipping. As a consequence of the alloying action between the two metals, the coating produced by hot dipping is far from being simply a layer of zinc spread over the surface of the steel. An iron content of only a few hundredths of a per cent is required to affect the structure of zinc to such an extent as to render the change detectable under a microscope. From microscopic and electrical conductivity studies the limit of solubility of iron in zinc at ordinary temperatures has been found to be 0.02 per cent.[25]

Inspection of the equilibrium diagram of the zinc-iron system of alloys indicates the existence of two intermetallic compounds of iron and zinc having the formulas $FeZn_7$ (10.9 per cent iron) and $FeZn_3$ (22.16 per cent iron). It is to the presence of these compounds, particularly the former, that the departure of a zinc-dipped coating from pure zinc, in structure and properties, is to be attributed in large measure. The entire time elapsing during the hot dipping of a sheet, for example, from the immersion of the sheet in the molten zinc until the adhering metal coating solidifies after leaving the bath, is very short, usually only a fraction of a minute. The speed of a sheet passing through the coating machine is from 40 to 70 feet per minute, according to the thickness of coating desired and the thickness of the sheet used. Hence, conditions of complete equilibrium such as are implied in the diagram do not obtain in practice. The alloying action is very rapid, however. It has been shown[39] that in galvanizing wire, if the iron wire is in contact with molten zinc for as short a period as one-twentieth of a second, an alloy layer can be detected in the microstructure of the coating.

The equilibrium diagram is very useful in indicating the trend of the changes which may occur, although perhaps not their true magnitude. The structure of zinc coatings which have been annealed after the coating operation (Figure 15) corresponds much better to the structure under equilibrium conditions, upon which the diagram is based, than do ordinary, unannealed coatings. An iron-zinc compound of formula $FeZn_{10}$ has been reported[40] but it is generally considered that the existence of this compound has not been definitely established.

EFFECT OF THE HOT-DIPPING PROCESS ON THE BASE METAL

The reported detrimental effects on the base metal caused by hot-dipping are more properly to be attributed to some of the incidentals of the process than to the effect of the molten zinc itself. It is a well established fact that brittleness can be induced in steel as a result of pickling in acid although the change, in general, is of a temporary nature.[41] It has also been claimed [42] that inferior tensile and torsional properties found in some wire

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[39] Finkeldey, W. H., *Trans. Am. Soc. Testing Materials*, 26, Part 2, 304 (1926).
[40] Storey, O. W., *Met. Chem. Eng.*, 14, 683 (1916).

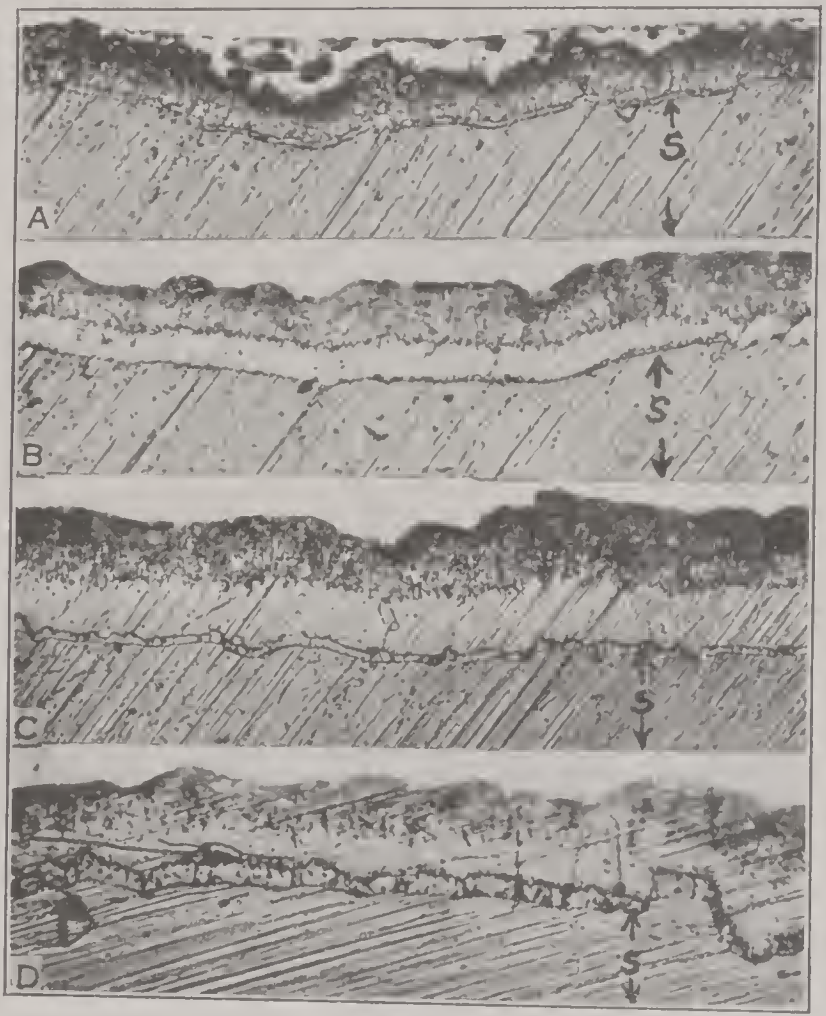

Figure 15.—Effect of Annealing Upon the Alloy Layers of a Zinc Coating. ×350[30]

A. Commercial hot-dipped zinc coating on an iron sheet which is indicated by weight of coating, 1.25 oz. per sq. ft.
B. Same after heating 2 hours at 350° C. Note prominence of the alloy layer.
C. Same as "A," after heating 4 hours at 350° C. Note how the thickness of the second alloy layer has increased.
D. Same as "A" after heating 5 hours at 350° C. The coating consists essentially in two alloy layers; the outer one corresponds rather closely to $FeZn_7$ in composition; the inner one, to $FeZn_3$.

coated with zinc by means of hot dipping were to be attributed to hydrogen retained by the metal. No well substantiated case of this kind has ever been reported, however. The greater part of the hydrogen in the steel to which the brittleness is usually attributed is driven off at a rather low temperature, approximately 200° C. (392° F.), so that it is extremely improbable that, at the temperatures employed in the hot-dipping process, an amount great enough to affect the mechanical properties of the metal would remain in the steel. The results given in Table 4[43] on samples of wire of the same reel are representative of the changes in the mechanical properties of the base metal which may be expected as a result of zinc dipping.

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[41] Langdon, S. C., and Grossman, M. A., *Trans. Am. Electrochem. Soc.*, 37, 543 (1920); Polansky, V. S., *Forging—Stamping—Heat Treating*, 10, 267, 298, 350 (1924); Edwards, C. A., *J. Iron Steel Inst.*, 110, 9 (1924); Williams, R. S., and Homerberg, V. O., *Trans. Amer. Soc. Steel Treating*, 5, 399 (1924); Alexejew, D., and Polukarow, M., *Z. Elektrochem.*, 32, 248 (1926).

[42] Winter, H., *Rev. Métal*, 7, 1064 (1910).

Table 4.—Strength of Wire Before and After Zinc-Coating.[43]

Electroplated[1]			Hot-dipped			No coating applied		
Spec. No.	Tensile Strength[2] (Kg./mm^2)	Elongation (%)	Spec. No.	Tensile Strength[2] (Kg./mm^2)	Elongation (%)	Spec.	Tensile Strength[2] (Kg./mm^2)	Elongation (%)
1	252	1.0	1	166	5.2	As received	199	2.6
2	249	0.9	2	168	5.8			
3	228	1.4	3	193	4.5	Tempered 300° C.	200	5.4
4	182	2.1	4	168	7.1			
5	201	1.3	5	140	6.4	Tempered 450° C.	131	3.6
6	207	1.6						
7	193	1.8						
8	198	3.0						
9	178	3.7						

[1] The electroplated wire was evidently tested soon after being plated.
[2] Conversion factor: for lbs. per sq. in., multiply by 1422.5.

Brittleness of malleable iron castings coated by zinc-dipping often causes a good deal of concern to manufacturers of such materials. It has been definitely shown, however,[44] that the heat-treatment effect incidental to the hot-dipping process, especially quenching the articles after they have been dipped, is responsible for the brittleness rather than any effect of the zinc *per se*. Certain features of the chemical composition of the malleable iron also seem to play an important part in rendering some irons more prone to brittleness than others. Studies have shown that the brittleness after galvanizing of cold-worked steel such as chain links, articles stamped out of sheet steel and structural steel angles is related to the extent of cold working and mechanical deformation rather than to hydrogen embrittlement.[45]

The annealing action of the molten metal bath, of course, cannot be avoided. Hence the hot-dipping process is not suitable for coating articles of which the properties would be seriously impaired by the hot metal, such as springs. The amount of such work is very limited and such parts are usually small and lend themselves to electroplating.

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[43] Lange, W., *Z. Metallkunde*, 13, 161 (1921).

[44] Bean, W. R., *Trans. Am. Inst. Mining Met. Engrs.*, 69, 895 (1923); Marshall, L. H., *Bur. Standards Tech. Paper*, 245, (1923).

[45] Allan, J. C., and Geruso, R. L., *Heat Treating Forging*, 16, 70 (1930); Epstein, S., *Proc. Am. Soc. Testing Materials*, 32, (Part 2) 293 (1932).

Surface Appearance of Zinc-Coated Sheets After Storage

The surface appearance of galvanized sheets after being stacked together either in transit or in storage for a considerable time, especially in very humid atmospheres and near the sea, is often spoiled by the formation of a white bloom which is distinctly different from flux spots or similar defects arising in the dipping process. Such materials are not infrequently rejected upon receipt of the shipment although there is nothing in the literature on this subject to indicate that in general the change is anything more than a slight surface corrosion of the zinc coating. The presence of lead in the zinc coating is considered by some to contribute to this behavior. It has been shown that the attack results from the development of oxygen concentration cells. In the inaccessible parts of the stack where the sheets are in intimate contact with one another, the oxygen concentration is less than in the more open parts. Hence, such portions of the metal surface are anodic with respect to those portions which have free access to the air. The zinc is corroded, therefore, as moisture condenses on the surface of the sheets, to form zinc hydroxide which constitutes the white bloom. Pronounced corrosion resulting in serious defects of the zinc coating from this cause is not common, however, unless the exposure conditions are very severe such as those reported by Argüelles[46] for stacks of galvanized sheets left exposed to the weather in the Philippines, in which case very severe corrosion resulted in the inner portions of the pack.

[46] Argüelles, A. S., *Philippine J. Sci.*, **11**, 177 (1916).

Chapter 5

Zinc Coating by Electroplating and Cementation

ELECTROPLATING

Electrodeposited zinc is one of the most widely used protective finishes for small articles. Coatings of this type are used also on metal screening, steel strip, pipe couplings, and wire. The application of electroplated zinc to sheet stock is, however, still very limited. A notable recent development has been the production of electrogalvanized round wire directly from the purified solutions of zinc-ore concentrates used in electrolytic zinc plants. An advantageous feature of this process lies in the heavier coatings which may be obtained. The process is being extended to sheet and strip stock up to 36 inches in width.[1] The demand for improved appearance in zinc coatings has led in another direction to the development of the so-called "bright" zinc coatings of such fine crystalline structure that light is reflected specularly from their surfaces. The metallic sheen of these coatings is quite unlike the diffuse gray appearance of the ordinary zinc electroplate.

Plating Baths

The electroplating of iron and steel with zinc for protection against corrosion was proposed in 1840.[2] An alkaline zinc cyanide plating bath was patented as early as 1855,[3] although baths of this type assumed little commercial importance until about 1916.[4] The first patent on zinc plating granted in this country was in 1862 [5] for a bath containing "sub" or "proto" sulfates and "sub"-acetates. The early commercial zinc plating was from acid sulfate or chloride baths and by 1900 the process was extensively used. At the present time the two principal types of baths used for zinc plating are the acid sulfate and alkaline cyanide solutions. The purified solutions of zinc concentrates used, as mentioned above, for wire plating, are essentially acid sulfate baths from which various metallic impurities have been removed.

It is owing to the high hydrogen overvoltage of zinc that it may be plated from acid solutions. Although satisfactory deposits may be obtained from neutral and even from ammoniacal sulfate baths[6] it is the general practice to maintain sulfate solutions slightly acid in order to obtain deposits free from basic salts.[7] At high acidities considerable hydrogen may be deposited, particularly if impurities of low hydrogen overvoltage are present, producing thereby pitted or spongy deposits. Furthermore the tendency of zinc anodes to corrode upon standing in sulfate solutions results in a gradual reduction of acidity. It is common practice therefore to regulate acidity in the range of pH from 3.5 to 4.5 by the use of "buffers" such as sodium acetate or aluminum chloride or sulfate.[4]

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[1] Tainton, U. C., *Private Communication*, April 28, 1938.

[2] Sang, A., *Rev. Métal,* **9**, 1, 78, 160, 275, 343 (1912).

[3] Watt, A., "Electroplating and electrorefining of metals," rev. by A. Philip., 2nd ed., New York, D. Van Nostrand Co., Inc., 1911.

[4] Thompson, M. R., *Trans. Am. Electrochem. Soc.*, **50**, 193 (1926).

[5] Besley, C., U. S. Patent 36750 (1862).

Zinc sulfate ($ZnSO_4 \cdot 7H_2O$) is usually employed for preparation of the sulfate plating baths. From 150 to 300 grams of this salt per liter (20 to 40 oz. per gal.) may be used. Ammonium or sodium chlorides or sulfates may be added to the bath to increase its conductance. In order to improve the throwing power of the bath and the appearance of deposits addition agents are generally added to sulfate solutions. Usually these are substances of organic nature such as glycerin, corn syrup, licorice, and starch, but aluminum sulfate[8] has been used.

Sulfate plating baths are usually operated at ordinary temperature, and at current densities from 1.5 to 3.0 amperes per sq. dm. (14 to 28 amperes per sq. ft.) It is claimed that current densities up to 33 amperes per square decimeter (300 amperes per sq. ft.) may be employed commercially provided zinc anodes containing mercury and aluminum are used.[9] In the Tainton process of wire plating, to be described later, current densities as high as 220 amperes per square decimeter (2000 amperes per sq. ft.) are employed.

Alkaline zinc cyanide baths possess much better throwing power than do acid sulfate baths[10] and are therefore preferable for plating irregular parts having recessed areas. The deposits are darker in color than those from sulfate solutions although it has been found that the use of small amounts of mercury in the bath and in the anodes produces brighter deposits. The use of mercury is also said to be an advantage in cyanide zinc baths to be used in plating cast iron.[7] Care, however, must be taken in the use of mercury in zinc baths for zinc deposits containing an excess of mercury have been observed to exude droplets of this metal from their surfaces in time.

Alkaline zinc cyanide baths are complex in nature and contain at least zincate $(ZnO_2)^{--}$ ions, zinc cyanide complex $[Zn(CN)_4]^{--}$ ions and of course zinc Zn^{++} ions. The solutions may be made up from zinc cyanide and sodium hydroxide or from zinc oxide and sodium cyanide. The desirable concentration of zinc (expressed in terms of $ZnCN_2$) is between 30 and 60 grams per liter (4 and 8 oz. per gal.) and it is essential to have present an excess of cyanide and hydroxide. Apparently the best results are obtained when the ratio of the normalities of the combined sodium cyanide and hydroxide to the normality of zinc cyanide is equal to about 2.[11]

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[6] Rogers, R. R., and Bloom, E., *Trans. Electrochem. Soc.*, 67, 299 (1935).

[7] Blum, W., and Hogaboom, G. B., "Principles of electroplating and electroforming," 2nd ed., p. 322, New York, McGraw-Hill Book Co. (1930). This text, which contains an authoritative description of plating operations, bath formulas, etc., has been freely drawn upon in the preparation of the present material. For greater detail the reader is referred to this text.

[8] Frölich, P. K., *Trans. Am. Electrochem. Soc.*, 49, 395 (1926); Wasilewski, L., and Weber, A., *Przemysl. Chem.*, 17, 259 (1933).

[9] Graham, A. K., and Kolupaev, P. C., *Metals and Alloys*, 7, 14 (1936).

[10] Horsch, W. G., and Fuwa, T., *Trans. Am. Electrochem. Soc.*, 41, 363 (1922).

Alkaline zinc cyanide baths are usually operated in the temperature range of 40-50° C. (104-122° F.) and at current densities from 2 to 3 amperes per square decimeter (19 to 28 amperes per sq. ft.) More recently it has been shown that excellent deposits may be obtained from alkaline cyanide baths at current densities as high as 6.6 amperes per square decimeter (60 amperes per sq. ft.) using anodes containing aluminum and mercury.[12]

Anodes

Zinc anodes are cast or extruded from metal of high purity obtained either by electrolytic refining or by retort refining of ores which are free from objectionable impurities. The presence of copper, tin, antimony, arsenic, nickel, cobalt and lead is undesirable particularly in cyanide baths. The use of aluminum and mercury in anodes has been mentioned in the previous paragraph. Some years ago the use of 2 per cent of mercury in zinc anodes was proposed,[13] and later it was claimed that the addition of both mercury and aluminum (from 0.3 to 0.5 per cent mercury and 0.5 to 2 per cent aluminum) to zinc anodes is advantageous in the operation of both acid sulfate and alkaline cyanide zinc baths.[9]

Plating Tanks and Mechanical Equipment

Plating tanks are made of a variety of materials, the more common of which are steel lined with rubber and wood usually lined with lead, rubber, asphalt, tar pitch, sulfur-sand mixtures, etc. For acid sulfate solutions, lead linings are most commonly used although rubber-lined concrete is finding favor.[14] The tanks for alkaline cyanide solutions are generally of iron or steel construction used without linings.

Mechanical devices and automatic equipment for zinc electroplating have been developed to a very high degree of efficiency so that very little attention is required for their operation. The equipment varies according to the materials to be coated, but most of it is of one or the other of two general types, which may be designated as the "barrel" type and the "conveyor" type.

For zinc-plating bolts, nuts, screws, nails, washers, and in fact, all small articles which do not need to be handled individually in the plating bath, the barrel method, or a modification of it, is used. A perforated barrel made of some non-conducting material is immersed in the solution of the zinc salts, the electrolyte, and enough of the articles, properly cleaned, to fill the barrel partially, are placed within. They are in contact with flexible metal conductors on the inside of the barrel and together they form the cathode of the cell. The anodes, of cast zinc, are hung in the solution just outside the barrel and sometimes partially encircle it. The barrel is supported in the solution in such a manner that it can be rotated about its longitudinal axis. As the plating process proceeds the barrel is slowly rotated so that the articles are "tumbled" over one another, constantly exposing new surfaces to the plating current, thus ensuring a relatively uniform coating. In the conveyor type of equipment, the articles are moved through the plating solution past the anodes by means of an endless screw or a chain conveyor on which they are hung. The conveyor with the suspended articles upon it constitutes the cathode. Usually in this method the articles after having been attached to the conveyor are carried in turn through the preliminary cleaning and washing tanks, the plating tank and the final washing baths so that no handling is necessary except to place them on and remove them from the conveyor.

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[11] Graham, A. K., *Trans. Electrochem. Soc.*, 63, 121 (1933).

[12] Graham, A. K., *Trans. Electrochem. Soc.*, 67, 269 (1935).

[13] Wernlund, C. J., *Trans. Am. Electrochem. Soc.*, 45, 273 (1924).

[14] Stimmel, B. A., Hannay, W. H., and McBean, K. D., *Trans. Am. Inst. Mining Met. Engrs.*, 121, 540 (1936)

For coating wire and wire products such as wire screen cloth, the process is also continuous. The wire passes in turn through the pickling and washing tanks, the plating bath and then through the final washing tank. As many as thirty wires, each from a separate reel, are passed through the bath simultaneously, and in order to permit the wire to be pulled through at a relatively rapid rate the plating tank must be made very long. For example, tanks as long as 150 feet are used for this purpose. Wire screen cloth is coated in an entirely analogous manner although it is often found advantageous to pass the screen up and down over a series of rollers to permit the use of smaller plating baths. In all the above cases, for any given set of plating conditions the thickness of the coating is determined by the length of time the articles are in the plating bath.

Electroplating of Wire

The zinc coating of round wire, telegraph wire, etc. by electroplating has received considerable impetus as a result of the improvements in the process made by U. C. Tainton.[15] Essentially the plating solution and the method of operation are those developed originally in connection with the electrorefining of zinc, but employing much higher current densities. Since 1933 this method has been in use for coating wire and a plant is now in operation rated at 250 tons of wire per day.[16] Whereas the weight of zinc coatings which can be applied to wire by the hot-dipping process seldom exceeds 1.2 ounces per square foot (0.002 inch in thickness) it is possible by the improved electrolytic process to obtain coatings of almost any desired thickness. Actually coatings of 0.8, 1.6 and 2.4 ounces per square foot are in commercial production.

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[15] Tainton, U. C., *Mining Eng. J.*, 126, 856 (1928); Tainton, U. C., and Bosquin, *Trans. Electrochem. Soc.*, 57, 341 (1930); Tainton, U. C., *Wire & Wire Products*, 11, 225, 243 (1936); *J. Am. Zinc. Inst.*, 18, 42 (1937); *Trans. Am. Inst. Mining Met. Engrs.*, 527 (1937).

[16] Cambria Plant of Bethlehem Steel Company at Johnstown, Pa.

The plating solution is derived from roasted zinc concentrates containing 50 to 60 per cent zinc and a wide variety of metallic impurities such as cadmium, copper, silver, lead, gold, iron, nickel, cobalt, manganese, aluminum, arsenic, antimony, silicon, calcium, magnesium, tellurium, etc.[17] These concentrates are dissolved in about 2 molar sulfuric acid,—usually the return-electrolyte from the cells following the removal of zinc which contains about 250 grams of sulfuric acid per liter,—and the impurities removed by various methods. The purified solution, as it goes into the plating cells, contains about 225 grams of zinc and from 200-270 grams of sulfuric acid per liter. The steel wire to be plated, after annealing by passing through a molten lead bath, is electrolytically cleaned in molten caustic soda and soda ash at 650° C. (1200° F.)[18] and then in acid solution. The electrodeposition of zinc is carried out at a temperature not to exceed 35° C. (95° F.) at current densities from 77 to 220 amperes per square decimeter (700 to 2000 amperes per sq. ft.) The anodes used in this process are lead containing 1 per cent of silver.[19] In one installation, a view of which is shown in Figure 16, plating cells are used which are 110 feet in length. There are in this case 12 wires in each cell and the wire speed through the bath is from 50 to 200 feet per minute depending upon the size of wire and thickness of coating desired. A heavy coating of froth is maintained on the surface of the bath to prevent excessive acid spray during the plating operation. The froth is obtained by the use of a small amount of a mixture of silicic and cresylic acids. Finally the plated wires are drawn through tungsten carbide dies for the purpose of smoothing and brightening the coatings.

Heavy coatings of zinc are being rapidly deposited on both wire and steel strip also from nearly neutral sulfate solutions containing a buffer and addition agents and using high-purity zinc anodes.[19a]

Excellent adhesion of the zinc coating is secured by this process. Coated wire, for example, can be drawn down almost indefinitely without any detachment of the zinc. A substantial tonnage of window screen is now made by coating No. 12 or No. 14 B & S gauge wire with four or five ounces of zinc per square foot, drawing this down to No. 31 or 32 gauge, and weaving it into screen.[20]

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[17] Weisselberg, A., *Iron Age*, 137, 34, May 21 (1936); Tainton, U. C., *Iron Age*, 138, 59, Aug. 6 (1936); Anon., *Steel*, 98, 40, May 18 (1936).

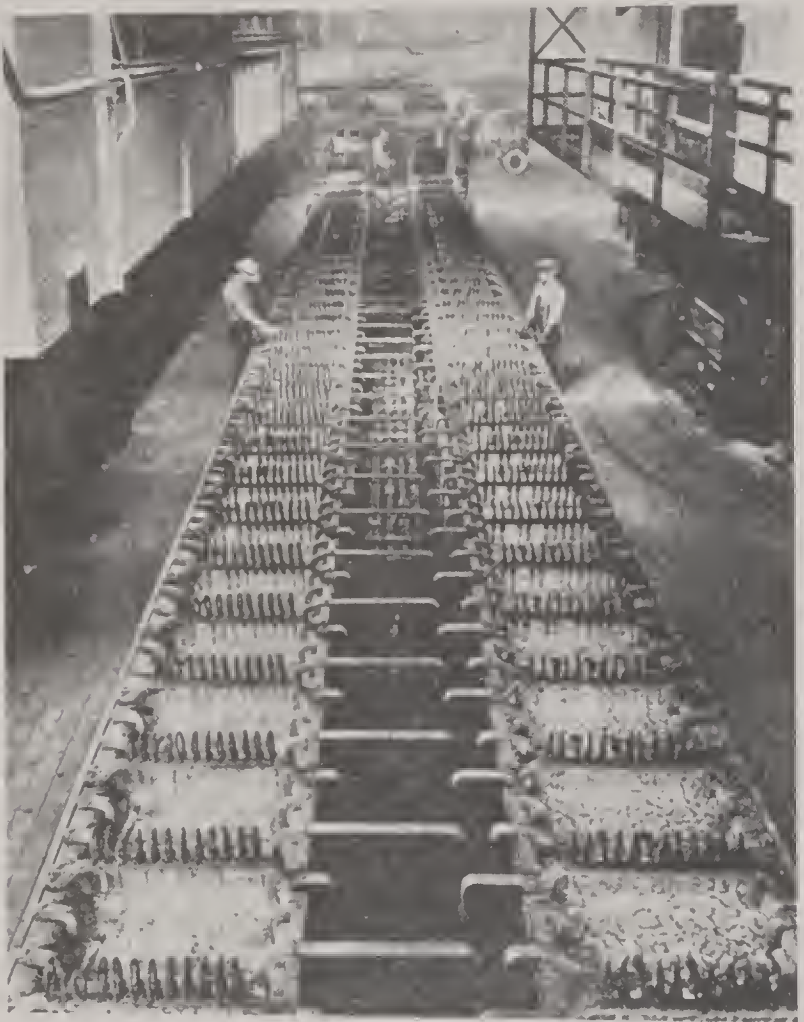
[18] Tainton, U. C., *Wire and Wire Prod.*, 9, 399 (1934).

[19] Tainton, U. C., British Patent 280,103, (April 29, 1927); Tainton, U. C., Taylor, A. G., and Ehrlinger, H. P., *Trans. Am. Inst. Mining Met. Engrs.*, 85, 192 (1929).

[19a] Lyons, E. H., *Iron Age*, Nov. 5, 1936; also Lyons, E. H., (Meaker Co.) *Private Communications*, Oct. 8, 15, 1938.

[20] Tainton, U. C., *Discussion, J. Am. Zinc. Inst.*, 18, 49 (1937).

This process is being applied on a pilot plant scale to sheet and strip stock up to 36 inches in width by the Bethlehem Steel Company at Sparrows Point, Maryland. It is expected that the results from the operation of the small plant will be used as a basis for the design of a commercial plant which will have in the first instance a capacity of about 100 tons of sheets per day.[1]



Courtesy American Zinc Institute.

Figure 16.—View of Electrolytic Cells in which Zinc is Plated on Wire. Each cell is 110 feet long and takes 40,000 amperes.[20]

"Bright" Zinc Electroplating

Within the past two or three years a number of processes have been patented for the production of bright zinc deposits. As mentioned previously the bright metallic lustre of these coatings is quite unlike the diffuse blue-gray appearance of ordinary electroplated zinc. As would be expected, the bright zinc deposits are but little affected by "finger-printing." However, it should be mentioned that in most exposures zinc corrodes at least superficially whether or not it is bright in the beginning. In other words, it has been observed that bright zinc tends in time to darken either uniformly over the surface or in localized areas.

Alkaline cyanide solutions form the basis of all the bright zinc plating baths. Addition agents in the form of organic compounds or soluble metal salts are employed in small proportions in all cases as a means of restricting the size of the crystals in the deposit. For example, there may be used for this purpose: methyl ethyl ketone; thiourea alone or with a salt of cobalt, iron or nickel;[21] thiourea with a salt of manganese or rhenium;[22] a reaction product of sulfuric acid and a terpene or terpene derivative;[23] or a flocculent colloidal substance, such as ferric hydroxide.[24] In the last-named case the bath is purified previously by the addition of a reducing agent, such as sodium bisulfite, sodium thiosulfate, phenyl hydrazine hydrosulfate, or formaldehyde, and the deposit obtained from the solution thus purified is said to be improved in ductility as well as in brightness.

The coatings obtained in the plating baths mentioned above are usually somewhat dull or brown in appearance and are finished by dipping in a brightening solution. A 1-per cent nitric acid solution may be employed for this purpose; but somewhat more satisfactory results may be obtained from a solution consisting of chromic acid to which small amounts of sodium sulfate and nitric acid [25] have been added.

Properties and Structure of Electroplated Zinc Coatings

An electroplated zinc coating is essentially pure zinc and, unlike coatings made by hot-dipping or cementation, contains no layers of alloyed iron. The average composition of such coatings is 99.85 to 99.90 per cent zinc,[26] and the product of the Tainton process is said to run 99.9975 per cent zinc. The nature of the impurities depends upon the composition of the anodes and the nature of the addition agents in the plating bath. Traces of lead, cadmium, copper and iron are likely to be the principal metallic impurities. Hydrogen to the extent of 0.055 per cent has been reported in freshly deposited coatings.[26]

Electroplated coatings will withstand severe bending or other mechanical deformation very much better than will other types of zinc coating of similar thickness. This is said to be particularly true of the high purity product applied to wire by the Tainton process and of the "bright" zinc coatings obtained at low current densities from highly purified cyanide baths.[24] Adherence tests made several years ago [27] in which the force required to separate the coating from the base metal was measured, showed the adherence of electroplated coatings to be nearly twice that of hot-dipped coatings. It is claimed that the adherence of plated coatings is materially increased by cathodic cleaning in fused caustic soda and soda ash.[28] The superior mechanical properties of zinc-plated coatings are, however, more properly to be attributed to the absence of the alloy layers than to greater adherence to the base metal. One interesting application of the improved mechanical properties of electroplated zinc coatings is the use of zinc-plated rivets for the fabrication of metal culverts and similar constructions. Even after the riveting operation, enough of the coating adheres to the head of the rivet to afford considerable protection against corrosion in service.

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[21] Hull, R. O., U. S. Patent 2,080,483 (May 18, 1937).

[22] Hoff, E. F., U. S. Patent 2,080,479 (May 18, 1937).

[23] Pine, P. R., U. S. Patent 2,029,387 (Feb. 4, 1936).

[24] Oplinger, F. F., U. S. Patent 2,075,623 (March 30, 1937).

[25] Meyer, W. R., U. S. Patent 2,088,429 (July 27, 1937).

[26] Schwartz, v., M., *Z. Elektrochem.*, 29, 198 (1923).

[27] Burgess, C. F., *Electrochem. Metal. Ind.*, 3, 17 (1905).

The crystal size and form of electrodeposited zinc coatings vary within wide limits according to the conditions of deposition. With very low current density zinc will be deposited from either a sulfate or cyanide bath in the form of numerous isolated nodules rather than as a continuous layer.[4] At very high current densities pitting and rough deposits may result unless suitable precautions are taken for the elimination of impurities from the solution. Zinc coatings deposited from cyanide solutions have a very fine grain structure and a very smooth surface. The coatings obtained from sulfate baths, using addition agents, may approach those from cyanide baths in fineness of grain structure, and are much whiter and brighter in appearance. The ordinary deposits from both of these baths tend to darken in time and to finger-print. These disadvantages have been reduced in the so-called "bright" zinc deposits which are described on a previous page. Another method of preventing the finger-printing of zinc coatings which is practiced to some extent abroad, is the application of a clear lacquer to the freshly plated surface.

ZINC COATING BY CEMENTATION: "SHERARDIZATION"

Of somewhat less importance than hot-dipping and electroplating is the process of producing zinc coatings by cementation. The process is generally known commercially as "sherardizing," the term being derived from the name of the originator, Sherard Cowper Coles who discovered it about 1900.

It has already been pointed out that the alloying of metals by cementation was known many years before it was utilized commercially for the production of zinc coatings. The first patent for the production of metallic coatings by this means was issued a hundred years ago to Miles Berry, an Englishman, who proposed to protect iron from corrosion by coating it with copper.[29] While zinc may be applied by sherardization to copper and other non-ferrous metals the present discussion will be concerned only with the coating of iron and steel by this method.

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[28] Tainton, U. C., *Wire and Wire Prod.*, 9, 399 (1934); Anon., *Steel*, 95, 22 (Dec. 24, 1934).
[29] Sang, A., *Electrochem. Met. Ind.*, 7, 485 (1909).

Outline of the Process

Sherardizing is particularly well suited as a process for zinc-coating small articles such as bolts, screws, nuts and small castings. It is not well adapted to sheets or wire, although the process in a modified form has been proposed for the zinc coating of wire.[30]

The articles to be coated, after cleaning, which as a rule need not be so drastic as for some other coating methods, are packed in zinc dust in a metal drum which may serve also as the shell of the furnace if the heating is to be carried out electrically. The container must be reasonably air-tight and be equipped with a tightly fitting cover. The container together with its contents is heated either electrically by heating coils in its walls or by gas, and is slowly rotated during the heating. Care must be taken that the zinc-dust packing does not completely fill the container, so that as the drum is rotated a slight "rumbling" between the zinc dust and the articles to be coated may occur and intimate contact between the two may result. This feature of operation is important as the uniformity of the coating produced depends to a very large extent upon it. The character of the zinc dust used, particularly its iron content, and the temperature and period of heating, also have an important effect upon the coating produced. Fine zinc powder absorbs moisture rather readily, and on heating, hydrogen is said to be evolved.[31] The evolution of hydrogen by the heated powder is an advantage rather than otherwise as it reduces the chances for oxidation.

Commercial "blue dust," a by-product in the usual method for smelting zinc, is the material used generally, although a special form of zinc powdered to 200-mesh fineness is used to some extent in combination with the blue dust. The blue dust contains approximately 85 to 90 per cent metallic zinc, with 5 to 8 per cent of zinc oxide. In some of the earlier descriptions of the process it was proposed that inert materials, such as sand, be added to the zinc powder in order to prevent it from caking.[32] Apparently satisfactory coatings can be obtained using as high as 80 per cent quartz powder with zinc dust.[33] The addition of small percentages of naphthalene to the dust is said to prevent the formation of zinc carbonate.[34] The presence of iron powder lowers the rate at which the coating forms.[35] The practice of the most successful users of the process has not favored dilution of the zinc dust but rather the addition at intervals of small proportions of new dust to the used dust. The use of 10 per cent new dust and 90 per cent used material carefully freed from iron and oxide particles has been found to give excellent results.[36] Such a mixture of used and new dust has a metallic zinc content of 80 to 92 per cent.[37]

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[30] Sang, A., *Trans. Am. Electrochem. Soc.*, **20**, 259 (1911); Bradley, A. F., U. S. Patent 2,009,573 (1935).

[31] Johnson, A. R., and Woolrich, W. R., *Trans. Am. Electrochem. Soc.*, **21**, 561 (1912).

[32] Sang, A., *Electrochem. Met. Ind.*, **5**, 187 (1907); Hinchley, J. W., *Trans. Far. Soc.*, **6**, 133 (1911).

[33] Kesper, J. F., *Oberflachentech.*, **10**, 108 (1933).

[34] Sauri, A. J., *Quim Ind.*, **7**, 117 (1930).

[35] McCulloch, L., *Trans. Am. Inst. Mining Met. Engrs.*, **68**, 757 (1923); Kuroda, M., *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **16**, 125 (1931).

Effect of Temperature

The temperature at which the cementation process is carried out has a marked effect upon the rate of formation of sherardized coatings. This is shown in Figure 17 which compares the rate of coating of iron, nickel and

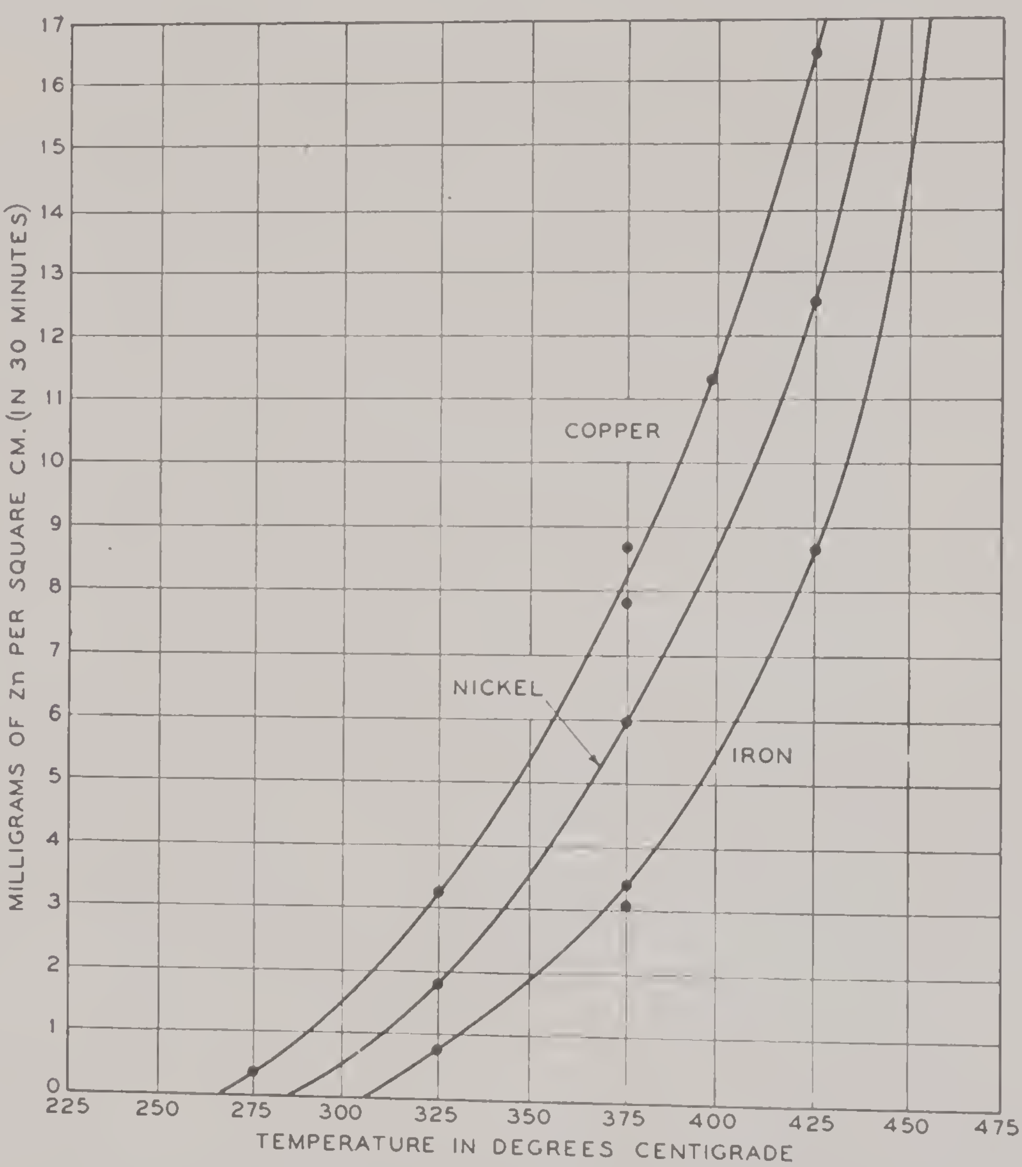

Figure 17.—Difference in the Rate of Coating Formation for Different Metals Heated in Zinc Dust.[31]

copper by zinc cementation.[31] It will be observed that points are given somewhat beyond the melting point, (419° C.) of zinc. Presumably a film of oxide surrounding each dust particle prevents their coalescence to form a melt of any appreciable size. It is possible, therefore, for the cementation process to be carried out considerably above the melting point of zinc. The appearance and properties of the coating vary with the temperature used. For most purposes a rather low temperature is favored, and 350 to 375° C. has been recommended as desirable. For spring stock and tempered articles temperatures as low as 250° C. have been used, although the rate of zinc deposition at this temperature makes the process rather unattractive commercially. The rate of coating at 375° C. is such as to provide commercially a coating of 15 milligrams per square centimeter (0.5 ounce per square foot) in 2 to 3 hours. The thickness of such a coating is approximately 0.001 inch.

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[36] *Iron Age*, 96, 1108 (1915).

[37] Storey, O. W., *Met. Chem. Eng.*, 14, 683 (1916).

The iron content of the coating is affected by the temperature employed in sherardization. Coatings produced at relatively high temperatures have a considerably higher iron content than those produced at lower temperatures, other conditions of operation remaining the same. The temperature which it is necessary to employ depends also to some extent upon the composition of the dust used. For example, it has been reported[38] that with dust containing 7 per cent iron the temperature must be maintained at 450° C (842° F.) in order to deposit a coating at the same rate that it is produced from pure zinc dust at 375°C. (707° F.) This also applies in the case of zinc-dross powder sometimes used in sherardizing.

The rate of zinc deposition is considerably reduced by the presence of a superficial film of oxide on the iron surface.[31]

Structure of Coating

The coating produced on iron by zinc cementation consists of fairly well defined layers if the outer rough portion of the coating, which appears to be built up mechanically, is disregarded. In coatings made at rather low temperature, for example, 350° C. or below, the greater part of the coating is a single-phase layer consisting of a solid solution of the compound $FeZn_7$ in zinc.[39] Although it is difficult to obtain a satisfactory chemical analysis of the coating at different depths below the outer surface, it has been observed in diffusion studies of the two metals that the average composition of the layer proceeding from zinc to iron ranges from 4.5 per cent iron to 17.7 per cent iron.[40] When iron foil is heated in zinc powder it has been shown that the minimum iron content of the product as a whole is approximately 6 per cent regardless of whether it was produced by heating at 365° C. for 2 days or at 415° C. for 45 days.[38] The average iron content of the principal layer of a sherardized coating runs usually from 8 to 10 per cent iron. Sometimes a second layer can be detected between the main layer of the coating and the iron base and, as the iron content of the coating is increased, generally as a result of a higher cementation temperature, this layer becomes more conspicuous. It is of a higher iron content and perhaps corresponds to the compound $FeZn_3$, indicated in the equilibrium diagram of the zinc-iron alloy system.

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[38] McCulloch, L., *Trans. Am. Inst. Mining Met. Engrs.*, **68**, 757 (1923).

[39] Arnemann, P. T., *Metallurgie*, **7**, 201 (1910).

[40] Rigg, G., *J. Inst. Metals*, **54**, 183 (1934).

It is to be expected that, as either the temperature or the period of cementation is increased, the iron content of the principal, or outer, alloy layer will increase in accordance with the equilibrium diagram for the iron-zinc system of alloys. The formation of a well defined second (iron-rich) layer adjacent to the iron base is hardly to be expected until at least the inner portions of the first layer are fully saturated with iron. This would imply a composition corresponding to $FeZn_7$ in much of this layer.

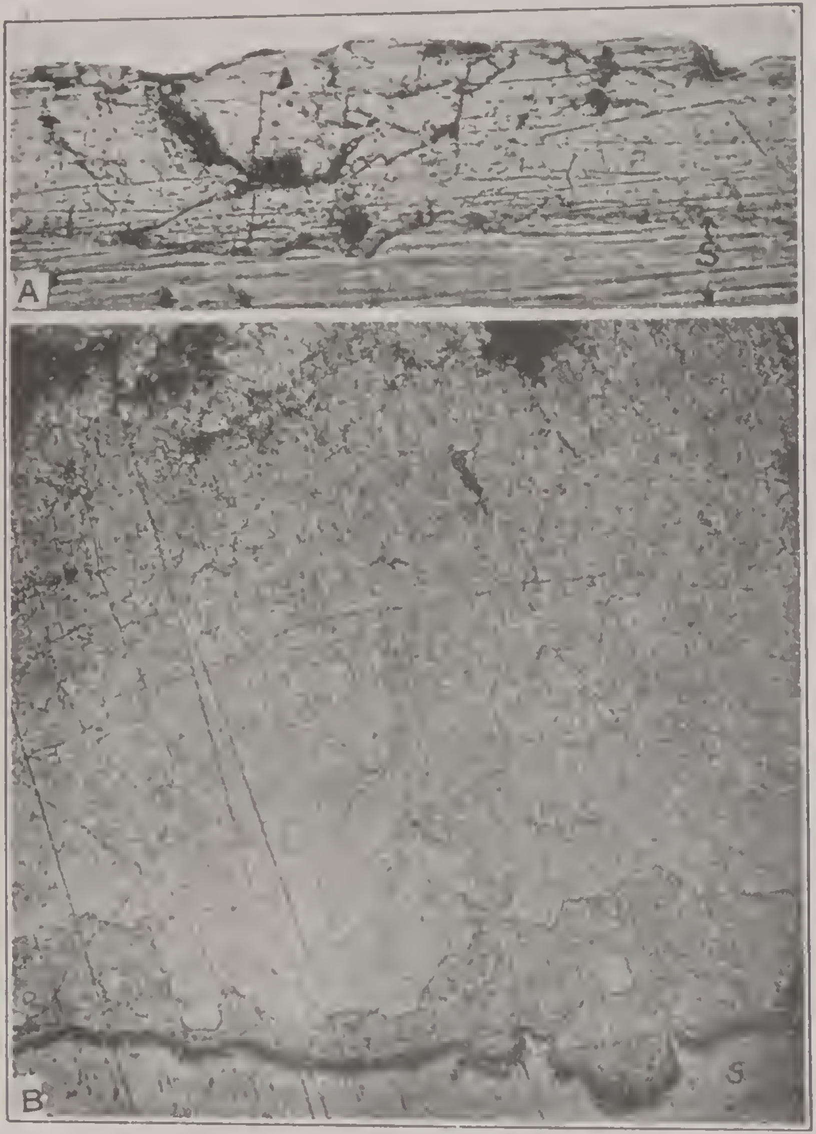

Figure 18.—Microstructure of Sherardized Zinc Coatings. [Rawdon, H. S., *Proc. Am. Soc. Testing Materials,* 18, pt. 2, 90 (1918).]

A. Cross-section of a Coating, 0.9 oz. per sq. ft., produced by sherardizing. S indicates the base metal. The fissured appearance is characteristic of coatings of this kind. The entire coating is made up of zinc-iron alloy. × 350.

B. Oblique section of a sherardized coating × 100. Note the two layers.

Figure 18 shows the microstructure of a sherardized coating. It will be noted that almost the entire coating is made up of one layer which has a characteristic fissured appearance. The outer part of this layer is rough and contains mechanically entrained inclusions, and on the inner side a very much thinner second layer exists.

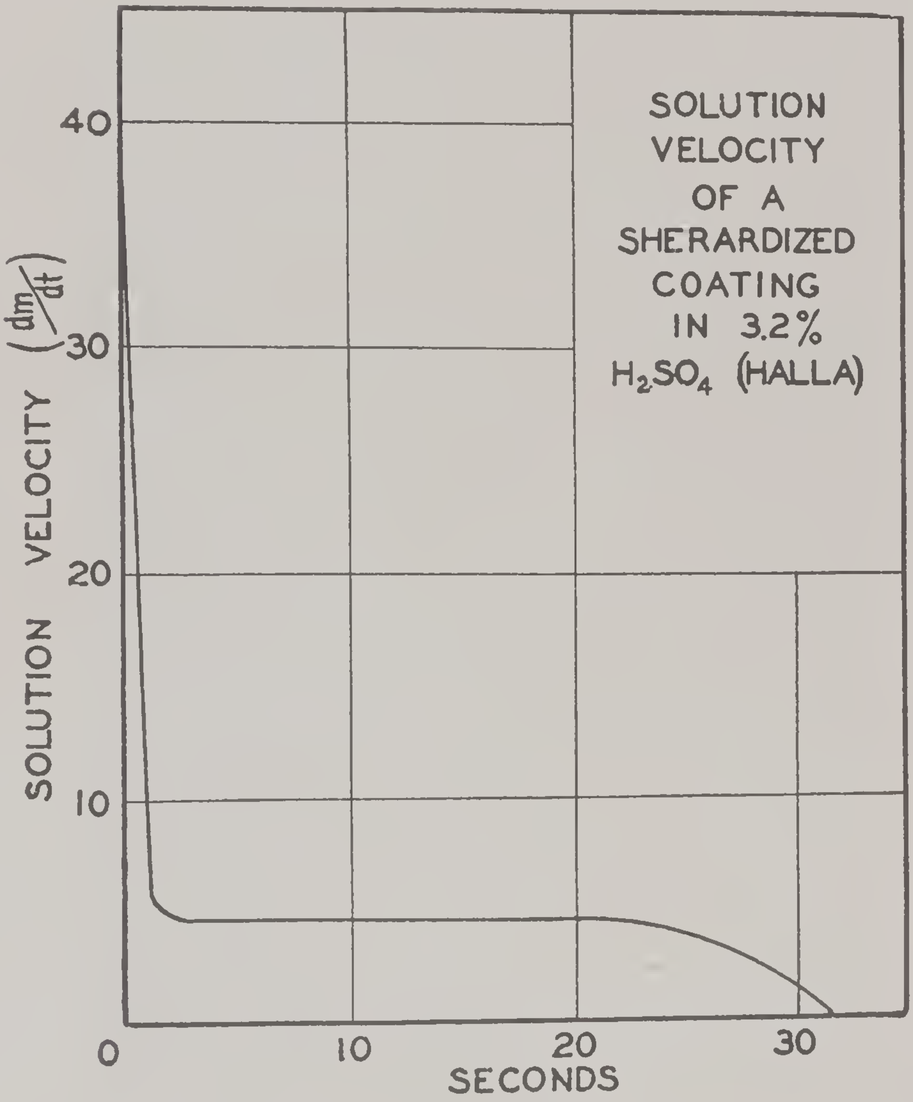

Figure 19.—Rate of Solution of a Sherardized Coating in Dilute Acid.[41]

Studies made of the "solution velocity" of sherardized coatings in dilute sulfuric acid confirm the conclusion based on examination of the microstructure that the bulk of any such coating is made up of a single and apparently uniform layer.[41] Nails sherardized under various conditions were used as material. Those used for the results in Figure 19 were heated for 3 hours at 365° C. in the zinc dust. From the loss-of-weight curves of the specimens immersed for given periods in the acid, the "solution velocity" was determined by graphical differentiation. It is seen that as the porous outer layer, high in entrained particles of zinc dust, is dissolved, the velocity of solution drops to a relatively low value and remains fairly constant for the rest of the coating, thus indicating uniformity of structure and composition for the coating as a whole.

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[41] Halla, F., *Z. Elektrochem.*, **19**, 221 (1913).

Mechanism of Zinc Cementation Process

The zinc coating of iron by sherardization occurs by means of diffusion in the solid state. There has been difference of opinion as to whether the mechanism involves condensation of zinc vapor on the iron surface prior to the diffusion process or whether intimate contact of zinc powder and iron is essential. Solid zinc has a relatively high vapor pressure, approaching 0.1 mm. of mercury at 350-375° C., and it is conceivable that zinc may pass through the vapor phase in going from the dust particles to the iron surface. It has been observed [31] that with relatively coarse zinc dust (100- to 150-mesh) more rapid deposition of the zinc coating is obtained than when extremely fine dust is used. For example, at 370° C., without tumbling, a coating was built up by the coarser dust about twice as rapidly as with the fine material. The coating, however, was quite porous and lacked the uniform, smooth surface characteristic of those made by the use of the very fine dust. Recent diffusion studies [40] of solid zinc and iron in the temperature range 350-390° C., have shown that alloying proceeds only from the points of physical contact and furthermore that diffusion occurs mainly, at least, by a process of migration of iron into zinc.

Unsuccessful attempts have been made to develop a commercial method of zinc-coating based strictly upon the action of zinc vapor.[42] It would appear that both contact of zinc powder and iron and the presence of zinc vapor are essential to successful sherardization.

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[42] Sang, A., *Proc. Engrs. Soc. West Penn.*, 23, 546 (1907); Cowper-Coles, S., *J. Soc. Chem. Ind.*, 28, 399 (1909).

Chapter 6

Protective Value of Zinc Coatings

NATURE OF PROTECTIVE ACTION OF ZINC COATINGS

Zinc is one of the more reactive metals. Free energy calculations show that it tends to corrode in the presence of moisture and air with the liberation of 71,500 calories for each gram atomic weight of metal converted into hydroxide.[1] Being readily corrodible zinc becomes coated with a film of corrosion products, the nature of which largely determines the eventual rate of corrosion. When a freshly prepared zinc surface is exposed to air of low or moderate humidities it combines directly with oxygen to form an oxide which is basally pseudomorphic with the underlying metal.[2] This densely packed oxide becomes converted after a few hours into the ordinary granular form of zinc oxide and from then on gain in weight with time follows a linear relationship.[3] That is, the rate of corrosion is determined by the rate of conversion of the pseudomorphic oxide into the normal zinc oxide,[4] the porous nature of the latter offering no impediment to the continuation of oxidation.

Under conditions of high humidity and atmospheric pollution the corrosion reactions of zinc become more complex and usually electrolytic in character. The corrosion products, formed when zinc was exposed in a Stevenson screen during the winter at the Royal Botanic Gardens, London, were found to be deliquescent at relative humidities of greater than about 75 per cent.[5] It is well known that such a deliquescent film accelerates corrosion by providing a moist conducting medium at the metal surface. At this location it was observed that zinc corroded nearly twelve times more rapidly in winter than in summer. In another test over a period of one year zinc exposed directly to the atmosphere corroded more than threefold more rapidly at Birmingham, an urban station, than at Cardington, a rural location.[5]

Rainfall removes about 75 per cent of the corrosion products from zinc surfaces if the results of tests in rural, urban and marine exposures are averaged together. The residual corrosion products remaining on the surface become basic in character and exert a retarding influence on corrosion. In highly industrialized or polluted atmospheres this basic film may not exist, a fact which may explain the more rapid attack experienced in such atmospheres.[6]

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[1] Brown, R. H., Roetheli, B. E., and Forrest, H. O., *Ind. Eng. Chem.*, **23**, 350 (1931).

[2] Finch, G. I., and Quarrell, A. G., *Proc. Phy. Soc.*, **46**, 148 (1934).

[3] Vernon, W. H. J., *Trans. Faraday Soc.*, **23**, 135 (1927).

[4] Finch, G. I., *Discussion Trans. Faraday Soc.*, **31**, 1116 (1935).

[5] Hudson, J. C., *Trans. Faraday Soc.*, **25**, 207 (1929). A Stevenson screen is a wooden box with a double roof and louvered sides employed by meteorologists to shelter their recording instruments from rain and direct sunlight.

The actual rate of corrosion of metallic zinc in the atmosphere under normal conditions[7] is in spite of these implications so low as to be practically negligible. For example, if the rates of corrosion observed at Birmingham and Cardington, mentioned above, are maintained it may be calculated that the probable life of a sheet of zinc 0.030 inch in thickness such as might be used for roofing would be about 80 years in the former locality and 260 years in the latter.[5] This relative incorrodibility of so reactive a metal lies then in the protective nature of the film of zinc compounds which adheres to its surface. It will now be of interest to consider to what extent this inherent characteristic of zinc of forming protective films is a factor in the protective value of zinc coatings applied to ferrous metals.

It is obvious that so long as zinc forms a continuous envelope around the metal to be protected the coated article will display in a large measure the properties of zinc. Commercial metallic coatings are, however, seldom free from porosity and minor defects which expose the underlying metal. This is true for zinc coatings particularly in thicknesses of less than about 0.002 inch. In the zinc-iron galvanic couple arising from this porosity or discontinuity of coating, zinc is the anodic or corroding element, thus providing protection to the bare iron areas. Faraday discerned the sacrificial action of zinc in protecting iron when the two metals are in contact. His observation is recorded in his diary under date of November 26, 1829, as follows:[8]

"Clean iron nails laid on clean sheet zinc in dishes with fluid so that both iron and zinc partly in fluid, partly in air. For the purpose of observing the protecting power of zinc over iron. After many days examined. Where water the fluid, action and oxidation both of iron and zinc—no protection of iron—no serious corrosion of zinc by its contact. Apparently not more than where wood intervening. But where sol. of common salt used there iron fully protected; no corrosion of it, great corrosion of zinc—when wood intervening then both corroded. Hence zinc can protect iron and iron destroy zinc in this saline solution, but not in pure water. An evidence this of the effect of chemical action, etc. in exciting electricity. The iron nail on the zinc in solution of salt had much free alkali adhering to it."

It is apparent from these considerations that the effectiveness of zinc coatings in the protection of iron depends upon both the inherent resistance of zinc and its anodic electrochemical relation to iron. The influence of the environment upon the corrosion resistance of zinc has been referred to in a previous paragraph. Zinc coatings reflect to an even greater degree the acceleration of attack produced by polluted atmospheres. In the following table is given the calculated probable life of a zinc coating of 2 ounces per square foot of surface of steel exposed to the atmosphere in various localities.[9]

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[6] Patterson, W. S., *Soc. Chem. Ind.*, 50, 120T (1931).

[7] That is, in the absence of factors conducive to pitting, such as contact with dissimilar metals or inert materials for periods of time.

[8] Faraday's Diary 1820-1862, Vol. 1, pp. 319-20.

Table 5.—Estimated Life in Years of a Galvanized Coating of 2 Oz. per Sq. Ft. of Surface (0.0033 in. thickness of coating) when Exposed to Atmospheric Corrosion.[9]

Locality	Type of Atmosphere	Approximate Life in Years
Overseas		
Khartoum	Dry tropical	150
Basrah	Dry inland	80
Apapa	Marine tropical	70
Singapore	Marine tropical	70
South Africa	Marine	20
England		
Cardington	Rural	25
Llanwyrtyd Wells	Rural	25
Bournville	Suburban	15
Wakefield	Industrial	10
Woolwich	Urban and industrial	20
Motherwell	Urban and industrial	15
Birmingham	Urban and industrial	8
Sheffield	Urban and industrial	5
Calshot	Marine	25
Southport	Marine	15
Doves Hole Tunnel	Railway tunnel	1

It will be observed that the highly polluted air of a railway tunnel is most destructive to a zinc coating which in country and seaside air protects iron for about 25 years. The attack in this case is electrolytic in character and the products of corrosion highly deliquescent. Absorption of sulfur dioxide as well as moisture by these products provides a medium of good electrolytic conductance at the metallic surface. Under these conditions electrolytic action would be expected to be rapid. This condition prevails to a lesser degree in urban and industrial localities where however rain tends to remove the greater part of the soluble products of corrosion which form in these atmospheres. In marine localities corrosion is also electrolytic in character but rate of attack is retarded by the protective nature of the basic corrosion products. At Khartoum and Basrah where conditions of low humidity prevail it seems probable that the mechanism of corrosion is of the direct oxidation type referred to in an earlier paragraph. Zinc coatings in the latter localities afford scarcely no electrochemical protection to iron. These atmospheres are not, however, very corrosive to iron.

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[9] Fourth Report (Special Report No. 13) of the Corrosion Committee, Iron & Steel Institute, p. 12, London, 1936.

PERFORMANCE OF ZINC COATINGS IN THE ATMOSPHERE

Distinctive Properties of Various Types of Zinc Coatings

Previous chapters have contained accounts of the preparation and general nature of various types of zinc coatings. It will be of interest in the discussion of the corrosion behavior of these coatings to recall their distinctive characteristics and relative behavior. In order of the tonnage of zinc consumed in their production hot-dipped coatings stand first, followed by electroplated, sherardized and sprayed coatings.

The surface of zinc-dipped coatings, particularly sheet stock, is characterized by macroscopic crystals known as spangles. The demand which has grown up in the trade for a well-spangled sheet is based on the pleasing appearance rather than the superior quality of such sheets, for there is no good evidence that spangle is any indication of quality.[10] The results obtained with a certain accelerated corrosion test indicate that the outer or zinc-rich layer of the coating is relatively very thin along the margin of individual spangles when these are of large size.[11] The thickness of this outer zinc-rich portion of the coating depends upon the circumstances of manufacture and is usually less than that of the so-called alloy layer. It contains about 0.02 per cent iron in solid solution. It is largely the character of the alloy layer which determines the physical properties of the coating. This layer, as previously stated, is composed in the main of two intermetallic compounds $FeZn_7$, in the larger proportion, and $FeZn_3$ at the coating-iron interface. Both of these compounds are hard and brittle as compared with zinc, and the coating of which they form the major part will necessarily show these same properties to a considerable extent. For example, heavy coatings in which the alloy layers are well developed will, as a rule, flake readily from the iron base when the latter is severely bent. The outer surface of the alloy layer is said[12] to have a pronounced effect upon the brittleness of a hot-dipped coating as a whole, as exhibited upon bending. Coatings in which the crystalline form of the alloy layer is well developed and the contour of its surface irregular owing to fern-like growths prove, under test, to be much more brittle than coatings of similar weight in which the contour of the alloy layer is smoother and more regular. There is evidence[13] which indicates that the physical character of the alloy layer, as modified by annealing, may affect the behavior of the coating upon bending, as much as does the total amount of alloy present. A process[14] of heat treating zinc-dipped wire as it comes from the galvanizing bath, known as "galvannealing," is said to produce heavy coatings with good

[10] Camp, J. M., and Francis, C. B., "The making, shaping and treating of steel," 4th ed., pp. 903-13, 968-982, Carnegie Steel Company, Pittsburgh, Pa., 1925.

[11] Rawdon, H. S., Krynitsky, A. I., and Finkeldey, W. H., *Proc. Amer. Soc. Testing Materials*, 24, pt. 2, 717 (1924).

[12] Finkeldey, W. H., *Discussion Trans. Am. Electrochem. Soc.*, 47, 201 (1925).

[13] Finkeldey, W. H., *Proc. Am. Soc. Testing Materials*, 26, pt. 2, 304 (1926).

[14] Schueler, J. L., *Trans. Am. Electrochem. Soc.*, 47, 201 (1925); U. S. Patent 1,357,907.

bending properties with no sacrifice in adherence. Upon deformation the stress in such coatings is probably relieved through the formation of numerous fine cracks. Cracking of a coating is not necessarily objectionable if peeling does not occur.[15]

Other factors affecting the ductility and adherence of zinc-dipped coatings are the purity of the zinc and the composition of the iron or steel base material.[15] "High Grade" zinc (containing less than 0.05 per cent lead and less than 0.01 per cent cadmium) is recognized as desirable for heavy-coated telephone and telegraph wire and for extra-heavy-coated sheets which are to be corrugated for such structures as highway culverts. Iron or low-carbon steel wire cannot without difficulty be coated with heavy ductile and adherent coatings. Steel wire stock of approximately 0.6 per cent carbon or rephosphorized steel of medium carbon content are suitable for the production of satisfactory zinc-dipped coatings.

Since much of the advantage of zinc as a protective coating depends upon its anodic nature with respect to iron, it is of interest to know to what extent this relationship is affected by exposure of the alloy layer as the outer zinc-rich portion of the coating is removed in the process of corrosion. Potential measurements show that the iron-zinc alloys which comprise this layer are anodic to iron, but by a lesser amount than is zinc in ordinary aqueous solutions. That is to say, these alloys protect iron, but under given conditions a lesser area of exposed iron will be protected from rusting. The inherent resistance of the alloy layer itself is comparable to that of zinc, so that in general the probable life of the coating is equivalent to that of an alloy-free zinc coating of the same thickness.

An electroplated zinc coating is essentially pure zinc. It may contain traces of copper, lead, cadmium and iron together with some inclusions, the nature of which depends upon the addition agents in the plating bath and the composition of the anodes. Hydrogen to the extent of 0.055 per cent has been reported in freshly deposited coatings.[16] In contrast to dipped coatings the structure of electroplated zinc is homogeneous, there being no alloy layer present. The crystal size and form may vary within wide limits according to the composition of the plating bath and the conditions of deposition.

Electroplated coatings will usually withstand mechanical deformation very much better than will other types of zinc coatings of the same thickness. In a certain type of adherence test[17] electroplated coatings were found to adhere with nearly twice the tenacity shown by zinc coatings made by the dipping process.

Cementation, or sherardized coating, consists essentially of a zinc-iron alloy of indeterminate composition, which, as would be expected, provides electrochemical protection to the iron base. It corresponds rather closely in composition and properties to the alloy layers of the zinc-dipped coating. As weathering occurs the coating gradually assumes a dark appearance, becoming finally a very dark gray if the iron content of the coating is not too high. Coatings high in iron usually show a red dusty surface upon weathering owing to the formation of ferric oxide. This reddish cast or stain sometimes creates the impression that the coating has been entirely corroded away exposing the ferrous base. It can be shown readily that such is not the case. There is evidence,[18] however, that such coatings are less resistant to atmospheric attack than those of lower iron content which form smooth black oxide finish upon weathering. That is, coatings containing about 15 per cent iron are appreciably less resistant to corrosion than those containing 11 per cent or less.[19] This difference in service life is to be attributed largely to the difference in the nature of the iron oxide film formed in the two cases rather than the relative electrochemical nature of the two. In the case of coatings low in iron, a closely adhering protective layer of iron oxide is formed, whereas the corrosion of the higher-iron layer results in loosely adhering flocculent rust which affords little if any protection to the metal beneath.

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[15] Finkeldey, W. H., *Met. and Alloys*, 2, 266 (1931).

[16] Schwartz, v., M., *Zt. Elektrochem.*, 29, 198 (1923).

[17] Burgess, C. F., *Electrochem. Met. Ind.*, 3, 17 (1905).

If the zinc dust used in cementation is high in iron, particles of this metal may be mechanically enclosed in the outer layer of the coating with the result that the coating will become rust-stained upon weathering.

Sprayed zinc coatings, like other metallic coatings applied by this process, consist in an aggregation of minute particles somewhat flattened and superficially oxidized. The coating as a whole is generally somewhat stratified, owing possibly to the repeated passing of the spray over the surface as the coating is built up. In spite of this, it possesses a high degree of coherence although it is less dense than electroplated coatings. There is no alloying with the base metal and the adherence of the coating is of a rather low order. Although the coating is somewhat porous in character, there are usually no pinholes extending through it to the base.

Comparative Life of Different Types of Zinc Finishes

Numerous laboratory tests to determine the relative protection afforded by different types of zinc coating have been based generally upon the resistance of such coatings to attack by acids, or salt solutions or else the development of pinhole rusting in distilled water. The principal value of such tests has been the information obtained concerning the uniformity of coatings in thickness. The early conclusions of these studies that electroplated zinc coatings are markedly superior to other types in corrosion resistance have not been borne out by atmospheric exposure tests.

The most comprehensive outdoor atmospheric corrosion test on zinc coatings is that carried out by the American Society for Testing Materials.[20]

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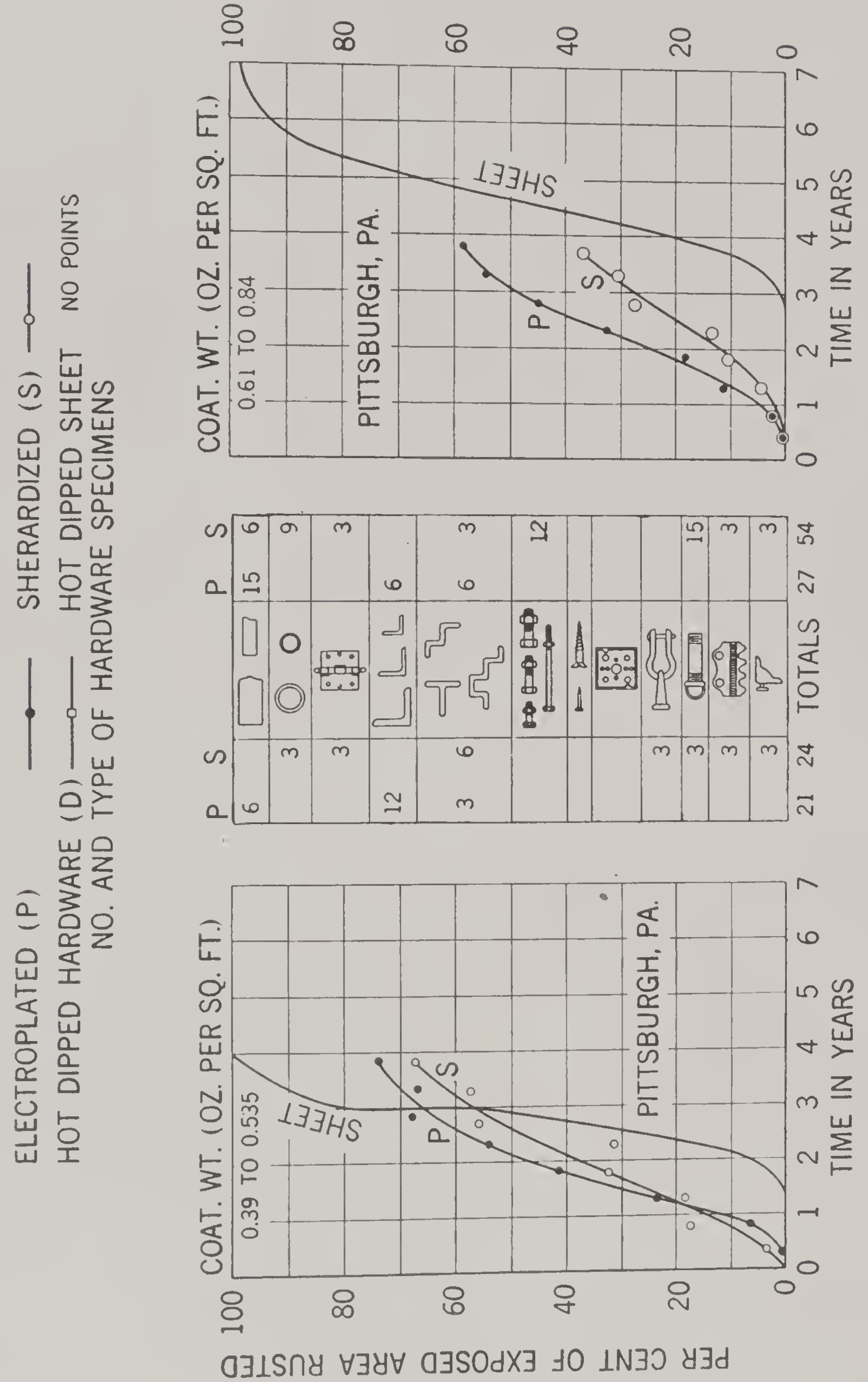
[18] Storey, O. W., *Met. Chem. Eng.*, **14**, 683 (1916).

[19] McCulloch, L., *Trans. Am. Inst. Mining Met. Eng.*, **68**, 757 (1922).

[20] For a full description of these tests see Reports of Subcommittee VIII, Committee A-5, on Field Tests of Metallic Coatings, *Proc. Am. Soc. Testing Materials*, **27**, (Part 1), 191, (1927); **29**, (Part 1), 149, (1929); **31**, (Part 1), 184 (1931); **33**, (Part 1), 156 (1933).


ELECTROPLATED (P)
SHERARDIZED (S)
HOT DIPPED HARDWARE (D)
HOT DIPPED SHEET NO POINTS
NO. AND TYPE OF HARDWARE SPECIMENS
PER CENT OF EXPOSED AREA RUSTED
COAT. WT. (OZ. PER SQ. FT.)
0.39 TO 0.535
SHEET
P
S
PITTSBURGH, PA.
TIME IN YEARS
0
1
2
3
4
5
6
7
0
20
40
60
80
100
P
S
6
3
3
12
3
6
3
3
3
3
TOTALS
21
24
P
S
15
6
9
3
6
6
3
12
15
3
3
27
54
COAT. WT. (OZ. PER SQ. FT.)
0.61 TO 0.84
SHEET
PITTSBURGH, PA.
P
S
TIME IN YEARS

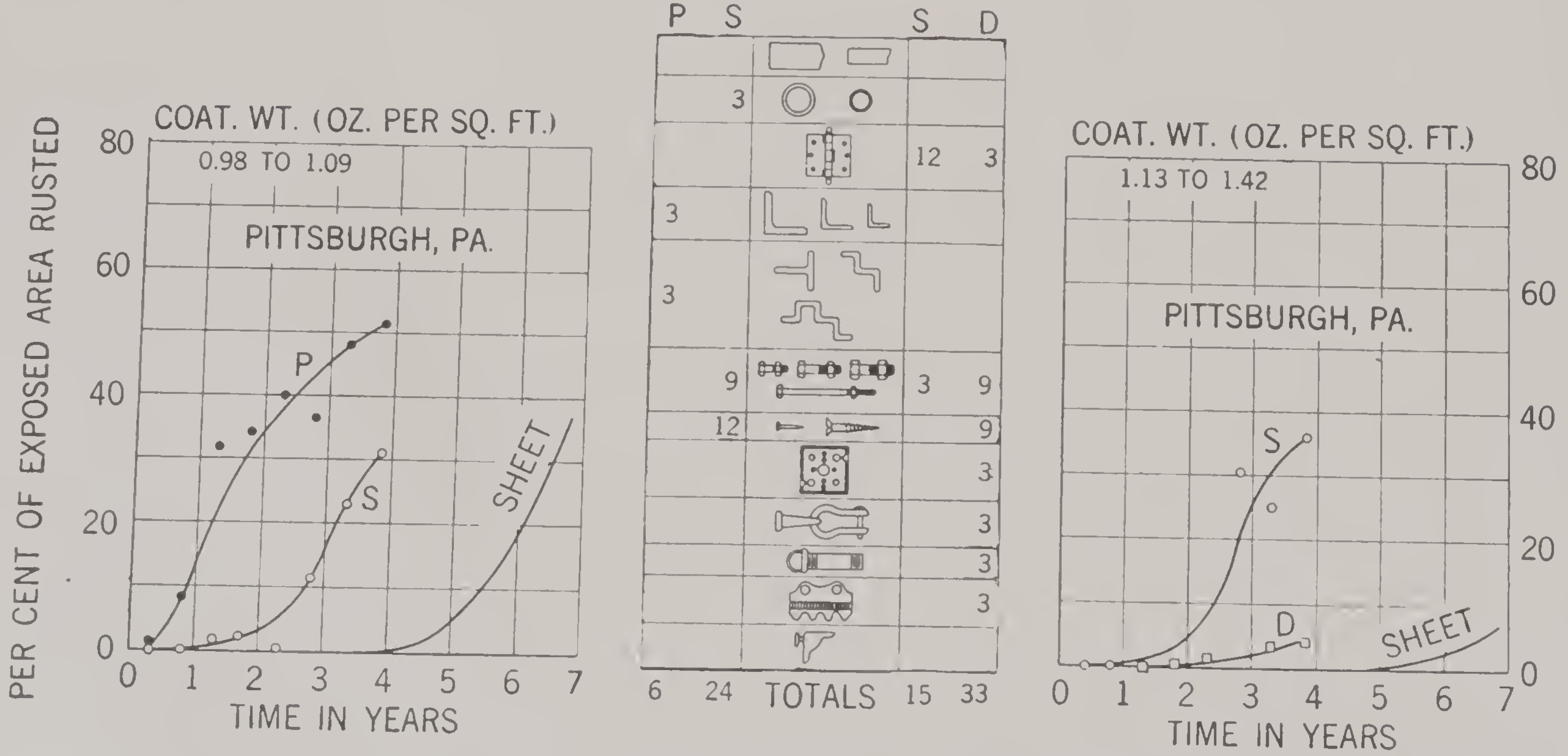


Figure 20.—Comparative Life of Zinc Finishes. (Pittsburgh Tests.) Hot-Dipped Sheet Coatings and Three Types of Zinc Coatings on Hardware.[21]

This general test of metallic coatings, which is still in progress, consists in the exposure of about 950 zinc-coated specimens on racks in the following five localities: Pittsburgh, Pa., Altoona, Pa., State College, Pa., Sandy Hook, N. J., and Key West, Fla. The first two locations are industrial in character; the third is rural, the fourth marine and industrial and the last, tropical marine. An analysis of the results of these tests after about six years of exposure has led to the conclusion that zinc-dipped, electroplated and sherardized coatings are "capable of being equally good in preventing rusting of the underlying iron provided adequate uniformity of coating is attained."[21] In Figure 20 the comparative life of hot-dipped sheet coatings, and hot-dipped, electroplated, and sherardized hardware are shown. The number and various shapes of the hardware articles are also represented.

It is apparent from an inspection of these results that uniformity of coating thickness is the principal factor in determining the relative life of different type coatings of a given thickness. As would be expected sheet stock upon which greater uniformity can be obtained gave the best performance, and electroplated hardware, where the distribution of coating in recessed areas is more difficult, made the poorest showing. Both plated and sherardized parts appear to be definitely inferior to those which were hot-dipped. Since the uniformity of coating should be somewhat similar for hot-dipped and sherardized coatings the results indicate that the sherardizing process is less effective than that of the hot-dipping process in the protection of iron. This confirms experience over a period of years in which it was found that malleable iron castings with sherardized coatings were less resistant to atmospheric corrosion than were similar castings with hot-dipped coatings.[22] It should be pointed out, however, that this experienced superiority of hot-dipped coatings is not reflected in the roof exposure test results obtained in New York City and shown in Figure 22.

In a corrosion test in which hot-dipped and electroplated specimens were exposed to the winter atmosphere in London[23] it has been reported that the former were the more resistant owing presumably to the formation of a less soluble, and therefore more protective, film of corrosion products. The total corrosion of the zinc-dipped coating at the end of 150 days was 2.97 milligrams per square inch and that of the electroplated coating 5.14 milligrams for the same area. However, in an exposure of about 180 weeks in the industrial atmospheres of New York and Pittsburgh it has been found that hot-dipped and plated zinc coatings of the same thickness furnish about the same protection.[24] It is understood that recent unpublished results from tests at Sandy Hook, N. J., and Washington, D. C., show

[21] Hocker, C. D., Symp. Outdoor Weathering of Metals and Metallic Coatings, *Am. Soc. Testing Materials*, page 1, 1934.

[22] Wolf, F. L., *Met. and Alloys*, 2, 341 (1931).

[23] Patterson, W. S., *J. Soc. Chem. Ind.*, 47, 313T (1928).

[24] Blum, W., Strausser, P. W. C., and Brenner, A., *Bur. Standards J. Research*, 16, 185 (1936)

0.001 in. of electroplated zinc to be superior to the same thickness of hot-dipped zinc at those locations.

A more detailed comparison[21] of the effect of specimen shape on the life of plated zinc is shown in Figure 21 where the results of electroplated angle and flat shapes separately are compared with hot-dipped sheets. The angle parts failed in the shortest time, and the flat parts in most cases are somewhat less durable than sheet stock.

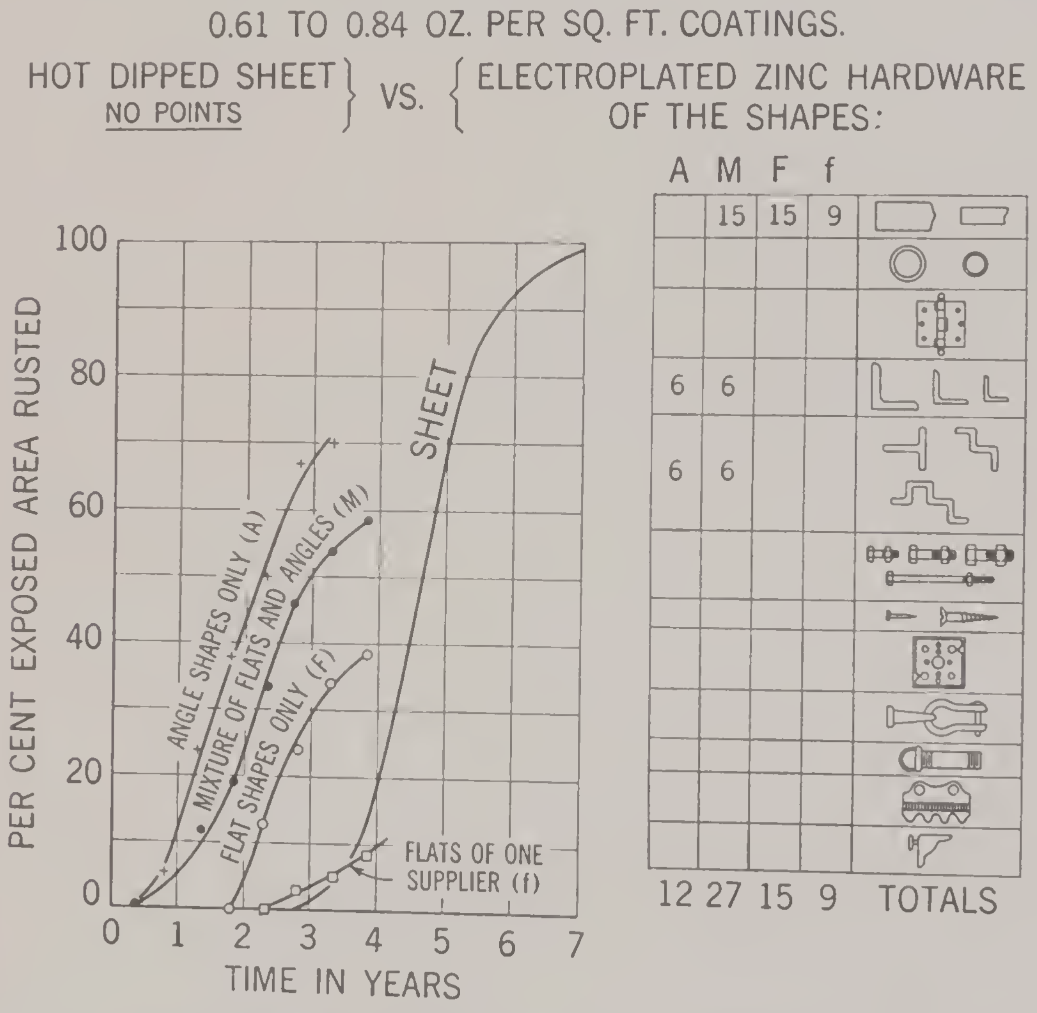


Figure 21.—Comparative Life of Zinc Finishes 1.06 to 0.84 oz. per sq. ft. Effect of Specimen Shape on Life of Plated Zinc.[21]

Apart from the lack of uniformity of the hardware parts it is possible that the surface curvatures of some of these parts is a factor affecting rate of corrosion. It has been shown,[25] for example, in studies of the corrosion of zinc-coated wire for a period of 6 months, that where the wire diameters in inches were 0.015, 0.06, 0.12 and 0.5 the weight losses were in the order 46, 24, 19 and 10 milligrams per sq. in. respectively. Similarly, whereas the rate of corrosion of hot-dipped and sherardized coatings on steel tubes in the New York City atmosphere is approximately 3.5 milligrams per square centimeter per year, based on an exposure period of 2.5

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[25] Mears, R. B., *Bell Lab. Record*, 11, 141 (1933).

years, the rate of similar coatings on flat panels is about 2.5 milligrams per square centimeter for the same period.[26]

The electroplated parts exposed in the A. S. T. M. tests were plated, it is understood, in acid sulfate solutions. It is well known that in general zinc coatings produced in this type of bath are somewhat less uniform in thickness than those obtained in alkaline cyanide baths. Moreover the actual rate of corrosion of sulfate zinc coatings in New York City air is reported to be about 1.5 times greater than that of coatings made in the alkaline cyanide solution.[27] This difference is shown in Figure 22 which contains the results of this test (curves 6 and 7) for a longer period of time, as well as other data to be discussed later. In a more recent and somewhat more comprehensive test, which has not been completed as yet, no consistent difference in the behavior of deposits from cyanide and acid-sulfate baths has been found.[24]

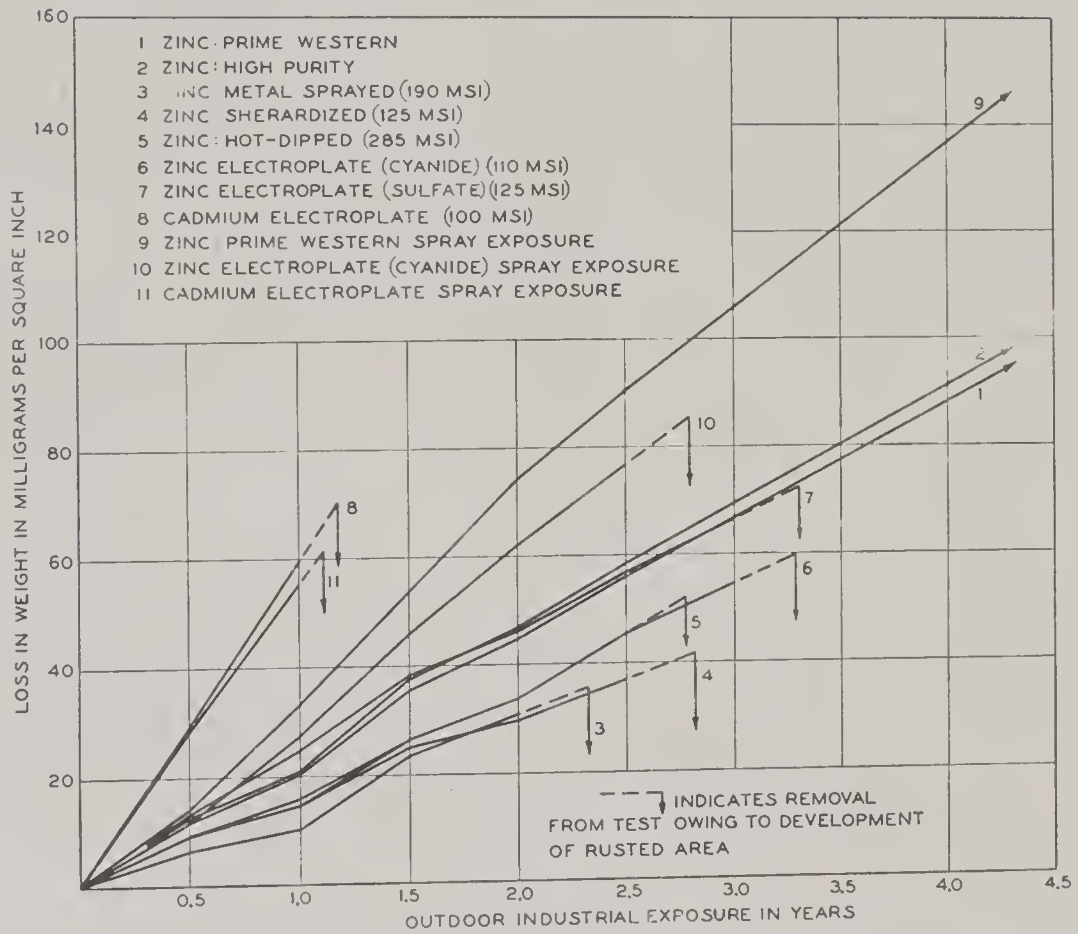

Fig. 22.—Rates of Corrosion of Zinc and Zinc and Cadmium Coatings (Average of 3 Samples).[27]

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[26] Hippensteel, C. L., Borgmann, C. W., and Farnsworth, F. F., *Proc. Am. Soc. Testing Materials*, 30, Pt. 2, 456 (1930).

[27] Hippensteel, C. L., and Borgmann, C. W., *Trans. Am. Electrochem. Soc.*, 58, 23 (1930).

Effect of Impurities upon Corrosion of Zinc Coatings in the Atmosphere

Atmospheric corrosion tests over a period of five years[28] indicate that antimony and copper are the only two common impurities in zinc which markedly affect corrosion. Antimony in proportions from 0.03 to 0.07 per cent accelerated attack whereas copper in proportions less than 0.06 per cent exerted a protective action. Variations in the cadmium, lead, or iron content had no appreciable effect upon corrodibility of the sheet zinc used, the average composition of which was: lead 1.12 per cent, cadmium 0.10 per cent and iron 0.03 per cent. The presence of small percentages of tin (0.005 per cent) or arsenic (0.09 per cent) did not influence the rate of atmospheric corrosion. Zinc coatings containing lead from 0.5 to 0.8 per cent and iron up to 5.3 per cent were similar in performance to coatings substantially free from these impurities after 30 years' service in a tropical country.[29] In the atmosphere of New York City, Prime Western (97.5 per cent zinc) and High Grade zinc (99.9 per cent zinc) corroded at approximately the same rate in a test carried on over a period of about four years. Figure 22 indicates that the purer grade is slightly more corrodible and this has been confirmed recently in tests of the American Society for Testing Materials.[30] Some evidence has been obtained[31] to the effect that the presence of lead in zinc actually retards the rate of corrosion in the atmosphere, although after a more prolonged exposure it appears that the influence of all the common impurities is negligible.

The results of the galvanic couple corrosion test sponsored by Committee B-3 of the American Society for Testing Materials throw light upon what may be expected to be the effect of metallic impurities in zinc when these impurities are present as separate phases. It will be realized, of course, that the relative areas of impurity and matrix metal may have, owing to polarization effects, some influence affecting the strict application of the couple results to the case under consideration.

The couple test was carried out by clamping together disks of seven common metals in all possible combinations of two metals and exposing these couples to atmospheric corrosion in nine locations. The metals employed were aluminum, zinc, iron, lead, tin, nickel and copper and the test sites were at LaJolla, California, Key West, Florida, and Sandy Hook, N. J., (marine); Pittsburgh and Altoona, Pa., (industrial); Rochester, N. Y., (urban); and State College, Pa., and Phoenix, Arizona, (rural). The results of this test for zinc coupled with the other metals and exposed at the above stations for a period of three years are shown in Figure 23.[32] The solid line through the group represents the average percentage weight loss of two disks of the same metal coupled together as a blank. The heavy dotted lines indicate the loss of weight of individual disks in the blanks. This percentage loss in weight of the blank is a measure of the normal corrosion rate of this form of specimen of the metal in the respective test exposures. The double cross-hatching illustrates the amount of corrosion of the zinc specimens induced by coupling with the metals shown.

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[28] Prost, E., *Rev. Univ. Mines Met.*, 6, 353 (1920).

[29] Argüelles, A. S., *Philippine J. Sci.*, 11, 177 (1916).

[30] Finkeldey, W. H., *Proc. Am. Soc. Testing Materials*, 38, Pt. 1, 195 (1938).

[31] Patterson, W. S., *J. Soc. Chem. Ind.*, 46, 390T (1927).

[32] Hippensteel, C. L., *Proc. Am. Soc. Testing Materials*, 35, Part 1, 167 (1935).

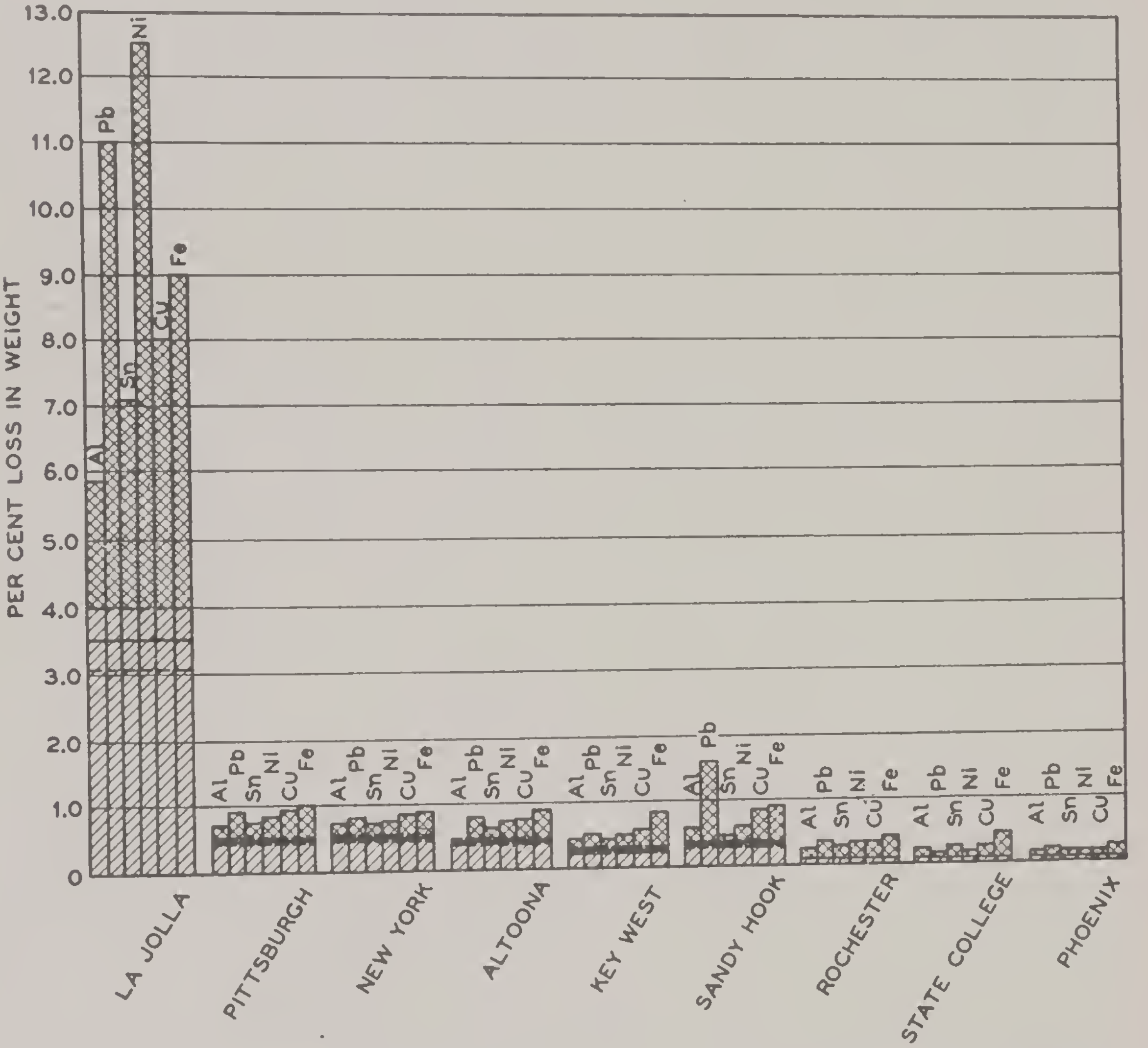

Figure 23.—Galvanic Couple Corrosion in Terms of Percentage Loss in Weight of Zinc after Three Years of Outdoor Exposure.[32]

The most striking result to be observed is the rapid rate of attack at LaJolla and the negligible amount of corrosion at Rochester, State College, and Phoenix. It will be seen further that all the other metals in almost all cases stimulated some galvanic corrosion of zinc. The least effect was obtained when aluminum or tin was the metal coupled with the zinc specimen. Aside from the information which this test provides concerning the effect of contact of other common metals with zinc, there is the definite indication that their presence as impurities in percentages beyond their solid solubility limits may be expected to accelerate corrosion of zinc at least in highly corrosive environments.

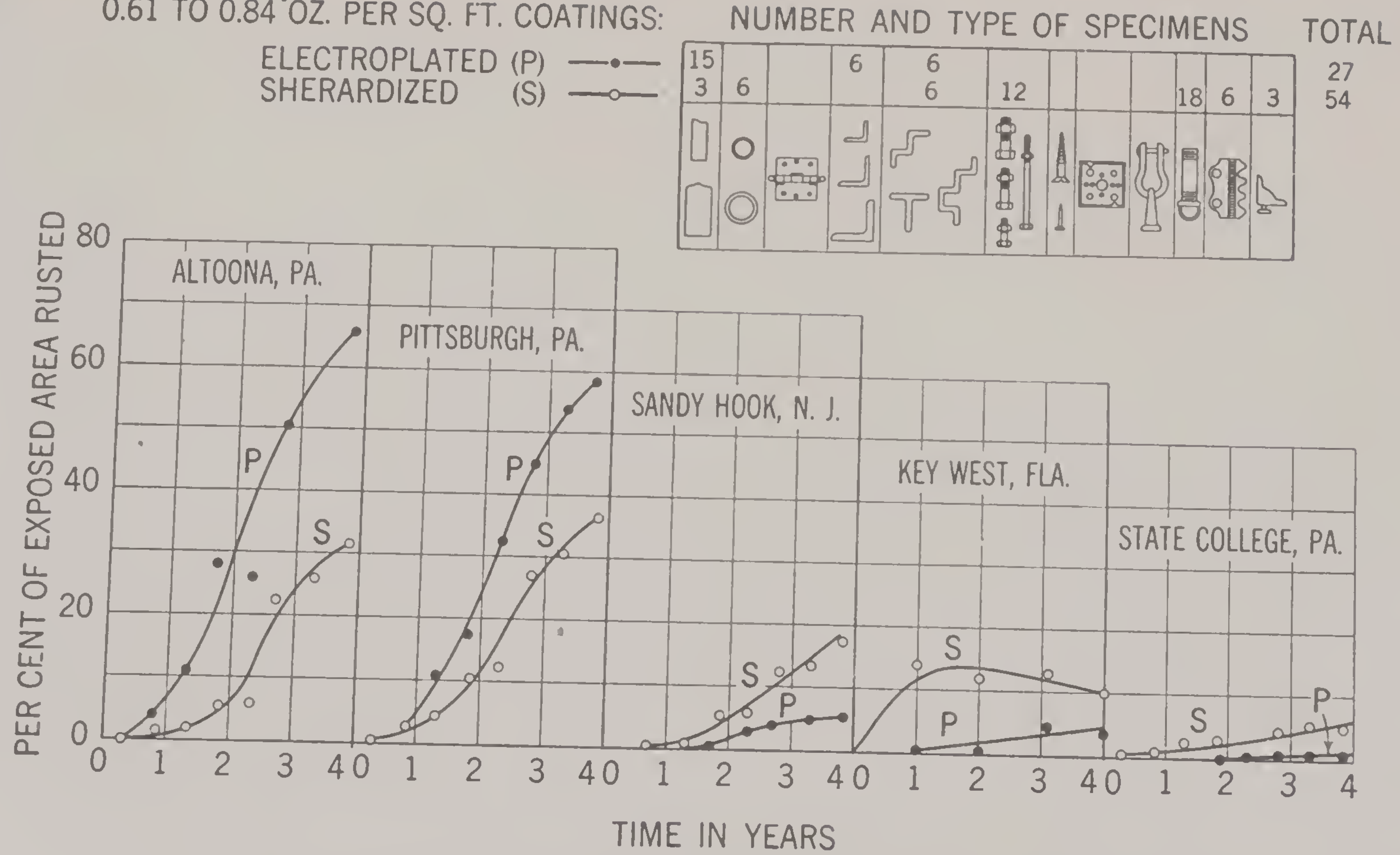

Figure 24.—Life of Zinc Finishes on Hardware, 0.61 to 0.84 oz. per sq. ft. Coatings. (Corresponding to 1.25 to 1.50 oz. per sq. ft. Sheet Coatings.)

Influence of Environment on Life of Zinc Coatings in the Atmosphere

The pronounced effect of environmental conditions upon the rate of corrosion of zinc and zinc coatings has been mentioned earlier in the present chapter in the discussion of the nature of the protective action of zinc coatings. The various atmospheric corrosion tests carried out in this country and abroad furnish abundant evidence on this point. A very direct comparison of the behavior of zinc coatings in industrial, rural and marine atmospheres has been obtained, for example, in the American Society for Testing Materials' studies. Results from these tests for the first four years of exposure of electroplated and sherardized coatings of moderate thickness are shown graphically in Figure 24.[21] It will be observed that corrosion is most severe in heavily industrialized atmospheres, intermediate in marine, and least rapid in rural exposures.

The early results of another atmospheric test [24] made chiefly on electroplated coatings are available. The coating thicknesses employed in this test were 0.0002, 0.0005 and 0.0010 inch and were applied to steel panels in both alkaline-cyanide and acid-sulfate plating baths. After an exposure of about 180 weeks most of the panels exposed in New York City and Pittsburgh were rusted over about 75 per cent of their surfaces. On the other hand, only the panels with the lightest weight of coating were appreciably rusted in the Sandy Hook, N. J. (marine), State College, Pa., and Washington, D. C., exposures. The heavier coatings were scarcely affected at the end of this period and it will require further exposure to reveal the relative severity of the latter locations.

It has been pointed out that there is an apparent correlation between the rate of corrosion of zinc and the extent of the pollution of the atmosphere. Thus in tests of the corrosion of zinc specimens at five experimental stations after an exposure of one year, the values for metal corroded and total solids deposited from the atmosphere were as follows:[33]

	Cardington	Bournville	Southport	Wakefield	Birmingham
Total Solids Deposited in grams/100m^2/month	407	549	528	793	1210
Rate of Corrosion of Zinc in mils/year	0.115	0.193	0.203	0.260	0.383

It will be recalled that Cardington is a rural location, Bournville, suburban, Southport, marine, and Wakefield and Birmingham industrial regions. This approximate correlation, interesting as it is, can scarcely give assurance that the value for total solids in an atmosphere will be a reliable index of corrosivity. Even in this table it will be observed that the rate of corrosion at Birmingham is relatively greater compared with Cardington than it should be if both were strictly proportional to the total solids in the air.

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[33] Hudson, J. C., *Discussion*, Symp. Outdoor Weathering of Metals and Metallic Coatings, *Am. Soc. Testing Materials*, p. 45 (1934).

The nature of the materials polluting the atmosphere must be in general as important in determining the rate of corrosion as is the total solids content of the air. Gaseous substances, particularly sulfur dioxide, may exert as great an influence as do solid sulfates in rendering the film of corrosion products on zinc acidic in character and therefore soluble and nonprotective. Undoubtedly a rough parallelism may exist between the amount of gaseous and solid pollution in the atmosphere.

Rainfall is another factor which may affect the corrosion of zinc coatings exposed to an outdoor atmosphere. Since the relationship between this variable and pollution is complicated it is doubtful if any general correlation between rate of corrosion and these two factors can be given with any degree of accuracy.[34] However, for a given location it is reported[35] that a direct correlation was observed between the corrosion of zinc and rainfall over a period from August to May. The divergence of the corrosion and rainfall curves during the summer months, June and July, was attributed to the reduction in atmospheric pollution during this period. In New York City the application of a water spray to zinc-coated specimens on those days on which it did not rain increased the rate of corrosion of zinc by 30 per cent.[36] A comparison of the behavior of zinc and zinc coatings in the normal atmosphere of New York and under conditions of additional "artificial" rain produced by water-spraying is shown in Figure 22. For example, compare Curves 1, 6 and 8 for normal exposure with Curves 9, 10 and 11 respectively for spray exposure.

Rain is contaminated by soluble substances of the atmosphere and in this way reflects the prevailing character of the locality. It is well known that near the sea rain will be somewhat saline in nature, in limestone

Table 6.—Effect of Rain Water on Corrosion of Zinc in Various Localities.

	Woolwich	Llanwrtyd Wells	Calshot	Sheffield
Inches of rainfall	1.65	5.94	2.49	1.97
Average pH	4.8	6.5	6.9	4.3
Total soluble solids	548	269	411	324
Total insoluble solids	560	63	238	3133
Total solids	1108	331	650	3456
Sulfates as SO_3	163	32	37	86
Chlorides as Cl	35	78	133	88
Corrosion of Zinc in oz./ft.^{2}/year	0.089	0.071	0.079	0.344
Type of locality	Industrial	Rural	Marine	Heavily industrial

Note: All data for rainfall and solids, sulfates and chlorides are expressed as the mean of the average monthly values. The solid substances are given as the amounts deposited in grams per square decimeter.

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[34] See discussion by R. F. Passano, Symp. Outdoor Weathering of Metals and Metallic Coatings, *Am. Soc. Testing Materials, p.* 63 (1934).

[35] Patterson, W. S., *J. Soc. Chem. Ind.*, 40, 120T (1931).

[36] Burns, R. M., *Bell System Tech. J.*, **15**, 20 (1936).

regions, calcareous, and that in cities it will be acidic. It is perhaps of interest, therefore, to examine analyses of rain water from pollution gauges situated at four stations where corrosion tests on zinc were made and to record at the same time the values for corrosion. The table on page 105 contains data obtained from 1931 to 1936 at Woolwich, and for shorter periods at Llanwrtyd Wells, Calshot, and Sheffield.[37]

It will be seen from an inspection of these results that there is no correlation between rate of corrosion and amount of rainfall; nor is there any direct correlation between rate of corrosion and the total solids content of the air, although where there is a marked increase in solids content there is a correspondingly large increase in corrosion rate. The pH values obtained for the rain water samples at these four stations do appear, however, to be of significance. It was pointed out in the third paragraph of this chapter that zinc exposed to the atmosphere of highly industrialized regions may not develop corrosion products of basic character, which products, because of their low solubility ordinarily retard corrosion of the metal. In other words, it may well be that rain water of pH 4.3 at Sheffield is sufficiently acidic to prevent the existence of the protective basic film, whereas at Woolwich, where rain has a pH value of 4.8 (and a value of 5 is reported for isolated samples taken independently), this film may develop. At the rural and marine stations the markedly higher values for pH of the rain water ensure corrosion products of basic type.

Conclusions Respecting the Life of Zinc Coatings in Outdoor Atmosphere

The foregoing discussion has considered the factors inherent in the coating and prevalent in the surrounding environment which determine the corrosion behavior of zinc coatings in the atmosphere. In general, it may be concluded that in a given location the life of a zinc coating depends upon its thickness regardless of the method by which the coating is applied. This does not overlook the fact, which has been dwelt upon, that coatings fabricated by the various processes vary in uniformity and may not therefore afford equal protection when coatings of the same average weight are employed. That the life of coatings of comparable uniformity is directly proportional to thickness is well illustrated in Figure 25,[38] in which the per cent of exposed area rusted is plotted against time of exposure for zinc-coated iron and steel sheets exposed at Altoona and Pittsburgh, Pa., and Sandy Hook, N. J.

With respect to the influence of the external or environmental factors on life of zinc coatings it is quite clear that the constituents of the atmosphere in industrial localities, together with humidity and rainfall, are of the greatest importance. The chloride content of sea air apparently has a mild accelerating effect on the corrosion of zinc coatings, particularly in

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[37] Hudson, J. C., "Fourth Report of Joint Corrosion Committee of the Iron and Steel Institute, the British Iron and Steel Federation, and the Iron and Steel Industrial Research Council," p. 43, London, (1936).

[38] Passano, R. F., *Am. Soc. Testing Materials*, 35, Pt. 1, 167 (1935).

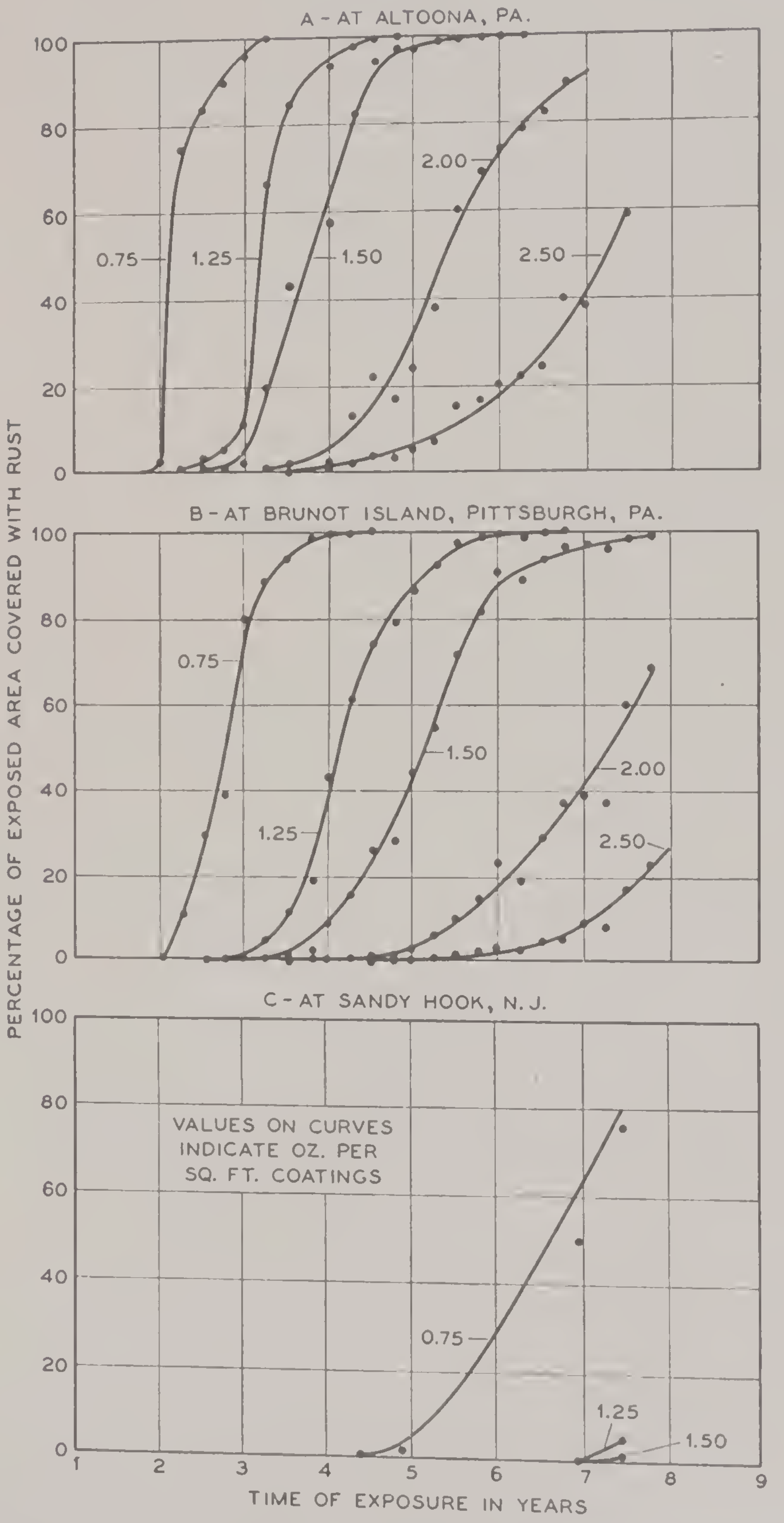

Figure 25.—Progressive Development of Rust on Zinc-Coated Sheets Exposed at Altoona and Pittsburgh, Pa., and at Sandy Hook, N. J.[38]

temperate climates. It is a curious fact, and unexpected, that the life of zinc coatings is appreciably longer in tropical marine locations than in temperate locations of the same type. The best performance of zinc coatings is found in the air of the open inland country. Where the climate is dry, even light coatings furnish protection to ferrous materials for long periods of time. In humid rural sections galvanized products of 1.0 oz. of zinc per square foot of surface (0.0018 inch in thickness) will last a generation.

Any estimation of the life of a protective coating requires a definition as to what is meant by the term life. Where appearance is not an important factor, the useful life of a protective coating is measured in broad terms by the period of time during which the coating prevents failure of the underlying metal. Failure is determined, of course, by the nature of the intended function of the coated article; if it is roofing it may be said to have failed when it becomes perforated and leaks; if it is fence wire it has failed when it breaks, etc. The thickness and corrosion resistance of the base metal are factors, therefore, in the useful life of zinc-coated articles. It has even been suggested [39] that, owing to the rapid corrosion of zinc-coated sheets experienced when moisture accumulates between the sheets in a pile, the life of a corrugated roof may depend largely upon the life of the base metal at the laps.

The definition of the life of zinc-coated iron or steel articles is usually expressed arbitrarily in terms of per cent of the surface showing rust. It may, however, happen that for some purposes a small amount of rust is relatively more significant than a large amount. A method of rating the quality of coatings on a percentage basis in which quality is not taken as proportional to the percentage of unrusted surface, but as a rough logarithmic function of it, has been employed in the atmospheric exposure tests on zinc and cadmium coatings carried on jointly by the American Electroplaters' Society, the American Society for Testing Materials and the National Bureau of Standards.[24] In this system, rusting up to 5 per cent of the surface is given a quality rating of 80 per cent, while surfaces which are on the average 75 per cent rusted are rated as zero in quality. The quality ratings (T) and per cent of surface rusted (R) after an exposure of about 180 weeks in five locations obtained in this test of zinc coatings are given in Table 7. It should be explained that the quality rating (T) is the average rating for the entire period and therefore does not agree directly with (R) the per cent of rust at the end of the period.

It will be observed from an inspection of these more discriminating evaluations of quality that the results are consistent with what would be expected from a knowledge of coating thickness and character of environment.

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[39] Passano, R. F., Symp. Outdoor Weathering of Metals and Metallic Coatings, *Am. Soc. Testing Materials*, p. 28 (1934).

Table 7.—Quality Ratings and Per Cent of Surface Rusted for Zinc Coatings. 180 Weeks' Exposure to Atmosphere.[24]

Description of Plating Bath	Thickness (mils) (in. × 10⁻³)	New York T %	New York R %	Pittsburgh T %	Pittsburgh R %	Sandy Hook T %	Sandy Hook R %	Key West T %	Key West R %	State College T %	State College R %	Washington T %	Washington R %
Electroplate	0.2	28	75	29	75	53	75	94	3	100	0	96	3
Standard	0.5	53	75	55	75	98	0	93	3	100	0	100	0
Cyanide Bath	1.0	74	55	91	28	98	0	92	3	100	0	100	0
Electroplate	0.2	30	75	22	75	55	75	90	3	100	0	89	60
Cyanide Bath	0.5	60	75	63	75	99	0	93	3	100	0	100	1
with Mercury	1.0	93	3	88	56	99	0	88	3	100	0	100	1
Electroplate	0.2	27	75	23	75	50	75	85	3	100	0	78	75
Sulfate	0.5	49	75	52	75	98	0	86	3	100	0	98	1
Bath	1.0	83	75	91	3	98	0	89	3	100	0	100	1
Electroplate	0.2	28	75	24	75	59	75	89	3	100	0	81	75
Sulfate Bath	0.5	52	75	55	75	97	1	87	3	100	0	100	1
with Dextrin	1.0	83	48	93	4	99	0	86	3	100	0	99	1
Hot Dip	0.9	76	75	86	75	98	3	85	3	100	1	100	1

A rather general estimate of the protective value of zinc coatings on ferrous metals exposed to the atmosphere may be derived from a summary of the experimental results cited in the foregoing discussion and others given elsewhere in the literature.[40] Table 8 contains what appear to be reasonable values for the expected life of zinc-coated products based upon information from these sources. It will be realized that these values are approximate in character and that in actual service exposure conditions may deviate from those considered typical of the atmospheres recorded in this table.

Table 8.—Estimated Life of Zinc-Coated Products in the Atmosphere.

Thickness in.×1000	Weight in oz./ft.^{2} of Surface*	Life in Years under Atmospheric Conditions					
		Rural	Tropical Marine	Temperate Marine	Suburban	Urban	Highly Industrial
3.6	2.00	50	40	35	30	25	15
2.3	1.25	35	30	25	20	17	9
1.8	1.00	25	20	15	12	10	7
1.1	0.60	10	8	7	5	4	3
0.66	0.37	7	6	5	4	3	2
0.44	0.25	5	4	3	3	2	1

* In the case of galvanized steel sheets the weight of zinc is specified in terms of total zinc on both sides of the sheet; *i.e.*, a 2-oz. sheet has 1 oz. of zinc per sq. ft. of surface. Consequently in estimating the life of galvanized sheet in the light of data given in this table, the specified weight and thickness values for the sheet should be halved.

Performance of Zinc Coatings in Indoor Atmospheres

Zinc coatings are used indoors for the protection of iron and steel articles where appearance is not a primary factor. It is well known that zinc coatings darken to an unpleasing gray color and that electrodeposited coatings in particular "fingerprint" and stain. The new "bright" zinc coatings provide a marked improvement from the standpoint of appearance although darkening to some extent and "spotting" may appear in some cases in these coatings.

The atmosphere indoors corresponds in a general way to that prevailing outside in a given locality. Variations in humidity and temperature, are, of course, somewhat less extreme and there is no rainfall indoors to dissolve and remove soluble corrosion products.

The manner in which zinc corrodes in the atmosphere when protected from rain was mentioned on the first page of this chapter. It was stated that in atmospheres of moderate humidities, such as prevail rather generally indoors, the corrosion of zinc, measured as gain in weight with time, follows a linear relationship after the first few hours. The slope of the weight-gain-time curve increases somewhat with humidity and with atmospheric pollution. At relative humidities above about 75 per cent this curve becomes slightly concave upward, indicating electrolytic action. Zinc of exceptionally high purity prepared by fractional distillation *in vacuo* and containing less than one part of impurity in ten thousand does not corrode or tarnish in laboratory air.[41]

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[40] Hubbell, J. P., and Finkeldey, W. H., *Trans. Am. Inst. Chem. Eng.*, 18, 51 (1926); also, Anderson, E. A., *Mech. Eng.*, 58, 799 (1936).

The corrosion of zinc coatings indoors is of the same general character as it is in outdoor exposures protected from rain. The presence of pores in the coating may result in the appearance of electrolytic action at somewhat lower relative humidities but usually there is little evidence of this type of attack. Indeed at low humidities indoors superficial rusting of iron is sometimes observed at pinholes in coatings, the thickness of which is of the order of 0.0002 inch. Porous zinc coatings do, however, in most instances provide adequate protection to ferrous articles exposed indoors and in so doing must undergo slow, although not very visible, sacrificial action. In general, it may be assumed that the protective life of zinc coatings indoors is at least fivefold greater than that of coatings of the same thickness exposed to the outdoor atmosphere in the same locality.

The darkening of zinc coatings with time does not affect their protectiveness. A coating of clear lacquer is sometimes applied to improve appearance of zinc-coated articles. This treatment produces a somewhat darker cast but arrests further change in this direction and prevents "fingerprinting."

The use of mercury proposed a few years ago [42] to improve the appearance of zinc-plated coatings resulted in some instances in the development of black spots on the surface. In other cases when appreciable amounts of mercury were deposited in the coating, actual droplets of mercury "sweated" out in time on the surface of coating and became very conspicuous against the darkening zinc areas. It is claimed that these difficulties with mercury have been overcome by using minimum and controlled quantities of this metal in the plating operation.

Performance of Zinc Coatings in Submerged Exposures

More work has been reported on the corrosion of zinc than on coatings of zinc under conditions of submersion or partial submersion in water and liquids. Most of this experience with zinc is, however, directly applicable to zinc coatings during at least that portion of the life of the coating when it is reasonably continuous. In submerged corrosion, electrolysis plays a larger part in the performance of the coating than it does in atmospheric exposure, and similarly corrosion products are even more important in determining the rate and character of corrosion under these conditions. Much of the material concerning the effect of type of coating and composition of coating on corrosion which is given in the preceding pages applies equally well to the behavior of zinc coatings in aqueous media.

Behavior of Zinc Coatings in Natural Waters

Zinc is not corroded to a measurable extent in pure water free from oxygen and carbon dioxide.[43] That some action does occur is evident from the fact that when zinc dust (which provides a large metallic surface area) is placed in water at ordinary temperatures for several hours, hydrogen is evolved.[44] When air or oxygen is present in water corrosion is accelerated owing to the depolarization of cathodic areas which ensues. After an interval of time, depending upon circumstances, the process becomes retarded by the formation of zinc hydroxide which occurs as a result of the reaction of zinc ions with hydroxide ions produced at cathodic areas. This product, hydrated to various degrees, is precipitated in gelatinous form, but may in time become crystalline in character. The rate of corrosion of zinc in pure water containing oxygen is generally controlled by the rate of diffusion of oxygen through this film of corrosion products. Zinc hydroxide is of a low order of solubility. If the water contains carbon dioxide, a slightly more soluble product, basic zinc carbonate, is formed. At higher pressures of carbon dioxide, the normal carbonate, still more soluble, becomes the normal solid phase. The effect of the presence of carbon dioxide in waters, then, is to increase their corrosiveness toward zinc and zinc-coated iron and steel. The corrosion products which can be assumed to be basic carbonates in most instances are less protective than zinc hydroxide.

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[41] Cyr, H. M., *Trans. Electrochem. Soc.*, 52, 349 (1927).

[42] Wernlund, C. J., *Trans. Amer. Electrochem. Soc.*, 45, 273 (1924).

[43] Bengough, G. D., Stuart, J. M., and Lee, A. R., *Proc. Roy. Soc., London*, A 121, 88 (1928).

The protectiveness of the film formed on zinc-coated cisterns and water pipes exposed to domestic waters depends upon many variables. Very likely the degree of hydration, crystalline structure, colloidal dispersion and the presence of other salts are all factors affecting the nature of the film. In general, although substances such as nitrates, and sulfates and chlorides in small concentrations increase the corrosiveness of water, it is well known that most domestic waters are less corrosive to zinc than is distilled water. Among the protective constituents present in natural waters are anions, such as carbonates and silicates, which form zinc salts of relatively low solubility and are precipitated in close contact with the metallic surface. Higher concentrations of sulfates appear to improve protection.

The more rapid corrosion of galvanized pipes and water tanks by hot water is attributable to the effect of temperature on the character of the corrosion products.[45] Up to 50° C. the rate of corrosion of zinc in aerated distilled water increases slowly with increasing temperature. At 53° C. the rate of attack increases abruptly, reaching a maximum at 65° C. above which it decreases rapidly. In the range from 20 to 50° C. the corrosion products are gelatinous and adherent, but above 55° C. they become granular and non-adherent. Beyond 65° C. the film of corrosion products becomes more dense and at 100° C., where rate of corrosion is small, the film is compact, glossy and very adherent.

The hydrogen-ion concentration of water and aqueous solutions has a marked effect upon their corrosiveness toward zinc and zinc coatings. This is well illustrated in Figure 26[46] in which the average overall penetration in centimeters per year is plotted against hydrogen-ion concentration expressed in terms of pH. It will be seen that the pH range 6 to 12.5 is characterized by the development of a stable film of corrosion products, the presence of which insures a low rate of corrosion, and furthermore, that on either side of this range the film is unstable and the corrosion rate high. The pH range of most natural waters used for domestic purposes is approximately 5.8 to 8.5, and were such waters free from carbon

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[44] Van Rijn, W., *Chem. Weekblad*, 5, 1 (1908).

[45] Cox, G. L., *Ind. Eng. Chem.*, 23, 902 (1931); *see also* Maconachie, J. E., *Trans. Electrochem. Soc.*, 66, 213 (1934).

[46] Roetheli, B. E., Cox, G. L., and Littreal, W. B., *Metals and Alloys*, 3, 73 (1932).

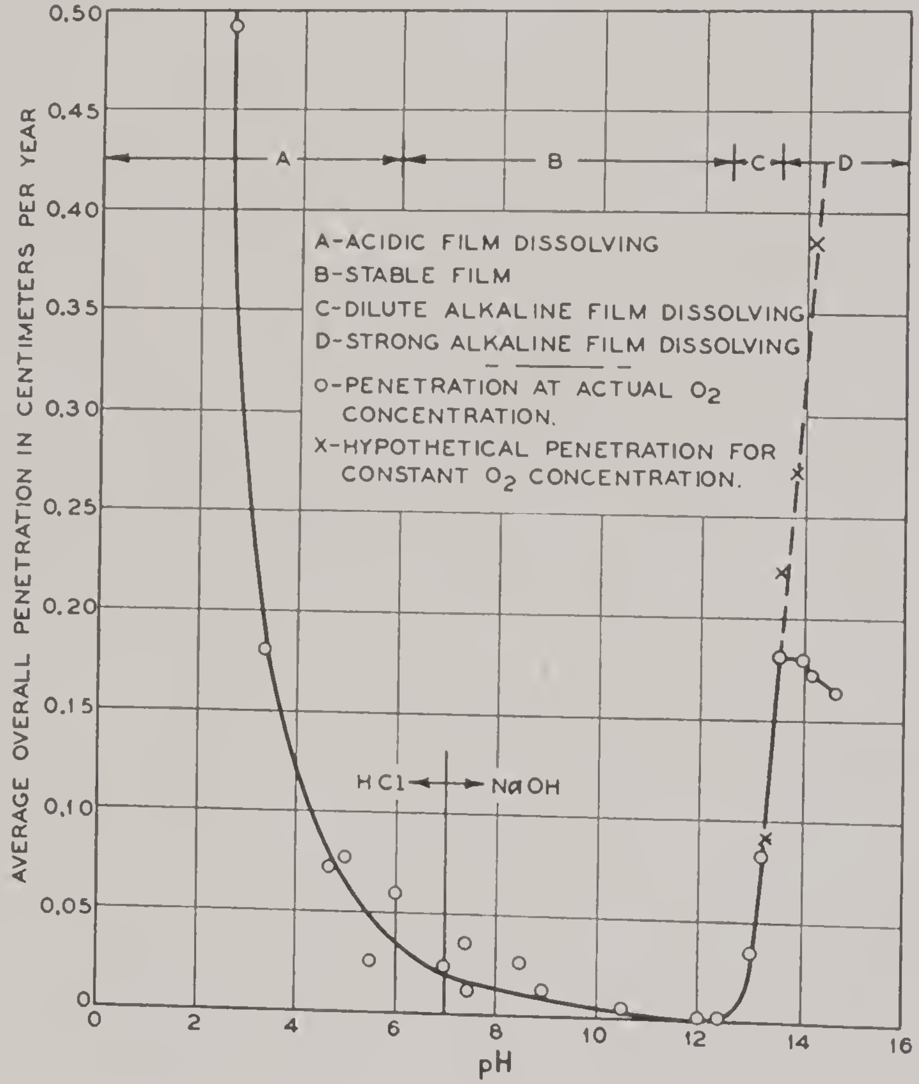

Figure 26.—Corrosion of Zinc as a Function of pH.[46]

dioxide, there would be little corrosion of zinc-coated pipes by them at normal temperatures. In general, the effect of the presence of carbon dioxide in waters will be to displace upward the curve given in Figure 26. Experience has shown that waters, the values of pH of which are below 6.5, corrode galvanized iron readily. This may be associated with the observation that the products of corrosion lose their crystalline character below pH 6.4.[47]

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[47] Baylis, J. R., *Amer. Water Works Assoc.*, 15, 598 (1926).

It should not be assumed that the nature of the film of corrosion products which forms on zinc is the only factor affecting corrodibility over the range of hydrogen-ion concentration under discussion. The oxygen concentration, for example, will vary. The depression shown in the actual rate of corrosion in the high alkaline range is the result of decreasing oxygen solubility. Another factor influencing rate of corrosion is undoubtedly the magnitude of the potentials of the corrosion cells at the metallic surface. The well known fact that zinc displaces hydrogen from both acids and alkalies suggests that the potential difference of the zinc-hydrogen cell is of somewhat similar magnitude over the range of hydrogen-ion concentrations from acid to high alkali. Actual measurements have shown that the potential difference of this cell from approximately pH 5 to pH 12 is about 0.3 volt.[48] In other words, the reduction of hydrogen-ion concentration over this range is accompanied, owing to the formation of zincate, $(ZnO_2)^{--}$ ions, by a corresponding reduction in zinc ion concentration.

The character of the corrosive attack of natural waters upon galvanized iron depends mainly upon the composition of the water. There is usually less pitting in galvanized iron pipes than in bare iron and steel pipes. In waters of pH 7.5 to 9.5 containing calcium bicarbonate but low concentrations of sulfates, chlorides and nitrates, the attack on zinc is negligible, owing to the formation of a carbonate film of high continuity and low solubility on the metallic surface. In waters low in temporary hardness (*i.e.,* calcium bicarbonate) or containing appreciable concentrations of sulfates, chlorides or nitrates, zinc-coated iron is likely to suffer a pitting form of attack.[49]

The thickness of zinc coatings in water pipes and storage tanks required to prevent "red water," or rusting of the underlying iron, depends upon the hardness of the water. In general, much thicker coatings are needed in soft water than in hard water.[50] There is evidence that in water of a given character there is a critical minimum thickness below which the protective life of the coating will be very short.[49] For example, in waters containing calcium bicarbonate the anodic dissolution of zinc is accompanied by the development of a film of basic zinc carbonate at anodic areas and a film of calcium carbonate on exposed iron areas. The formation of these films reduces the rate of solution of zinc. In other words, in any given water the thickness of the zinc coating should be sufficient to provide for the construction of a protective layer of corrosion products before all the zinc is dissolved. For the average city water supply, coating thicknesses of zinc of 0.0017 inch[51] and 0.002 inch[52] have been recommended as necessary for protection of iron and steel pipe.

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[48] Measurements by Dr. R. B. Gibney of Bell Telephone Laboratories.

[49] Britton, S. C., *J. Soc. Chem. Ind.*, 55, 19T (1936).

[50] See Evans, U. R., "Metallic Corrosion, Passivity and Protection," p. 574, London, Edward Arnold & Company, 1937.

[51] Friedli, *J. Chem. Zentr.*, 103, 3108 (1932).

[52] Naumann, *Gas u. Wasserfach.*, **77**, 403 (1934).

Corrosion of Zinc Coatings in Sea Water and Chloride Solutions

Steel armor wires used to support and protect submarine cables are zinc-coated. While it is true that additional protection in the form of asphalt and jute coatings, as well as of sea-bottom ooze, is provided in this exposure, the use of zinc seems to be a factor in the long life of these structures. From an inspection of galvanized wire-armored harbor cables after a period of submersion it is evident that the jute covering by enclosing the armor wire restrains free circulation of water and permits the stagnant solution near the surface of the wire to become saturated with zinc corrosion products. In other words, the presence of the jute covering is conducive to the formation of a protective film on the galvanized wire.

The exposure of bare zinc surfaces to sea water under conditions in which there was no restriction on the availability of oxygen gave greater evidence of attack. After a four-year exposure to sea water in the Bristol Channel a galvanized iron bar lost less weight than either iron or zinc bars employed in the same test.[53] The zinc specimen, while covered for the most part with a tenacious layer of corrosion products, displayed numerous dome-shaped excrescences beneath which the metal was pitted. Electroplated zinc coatings of the order of 0.0005 inch in thickness have been shown to afford considerable protection to aluminum and Duralumin over a period of 12 months when subjected to sea-water spray and intermittent immersion in sea water.[54] Laboratory studies on zinc foil immersed in sodium chloride solutions have shown that the maximum attack occurs in a solution containing 0.5 per cent sodium chloride and that in a 3-per cent solution of the salt, corresponding approximately to sea water, the rate of corrosion was lower and of the same order as in fresh water.[55] Incidentally the results which are obtained in corrosion tests of this type depend to a large extent upon the conditions under which the test is carried out.

Careful studies made of the corrosion of zinc in water and potassium chloride solutions,[56] under conditions of complete submersion in a vessel of given dimensions, show that in pure water and in solutions of chloride concentrations less than twenty thousandths normal, reaction occurs without the evolution of measurable quantities of hydrogen. At concentrations of potassium chloride greater than ten thousandths normal, hydrogen was always evolved except when highly purified zinc [57] was used; in the range ten thousandth to tenth normal potassium chloride, from 5 to 15 per cent of the total corrosion was accompanied by hydrogen evolution. Up to concentrations of fiftieth normal the rate of corrosion increases in proportion to the salt concentration, there being an excess of oxygen present. Beyond tenth normal concentration, the rate of corrosion decreases owing to the decreasing solubility of oxygen in the more concentrated solutions. In these studies the shape of the curve obtained by plotting rate of corrosion against salt concentrations depended to a large extent upon the conditions of the experiment.

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[53] Friend, J. N., *J. Inst. Metals*, **39**, 111 (1928).

[54] Sutton, H., and Sidery, A. J., *J. Inst. Metals*, **38**, 241 (1927).

[55] Friend, J. N., and Tidmus, J. S., *J. Inst. Met.*, **31**, 177 (1924).

[56] Bengough, G. D., Stuart, J. M., and Lee, A. R., *Proc. Roy. Soc., London*, **A 116**, 425 (1927); **A 121**, 88 (1928); **A 127**, 42 (1930); **A 131**, 494 (1931).

[57] Specimen furnished by the New Jersey Zinc Company prepared by fractional distillation and containing less than 0.0001 per cent of impurities.

The availability of oxygen is an important factor affecting both the rate and character of corrosion of zinc and zinc coatings in salt solutions. Laboratory tests made upon specimens of zinc partially immersed in potassium chloride solutions, instead of completely submerged as in the experiment described above, showed, in contrast to that experiment, that the rate of corrosion continued to rise with increasing salt concentration throughout the range of concentrations employed in the two investigations.[58]

The "water-line" in galvanized tanks and cisterns is a region often particularly susceptible to corrosive attack. With waters high in chlorides and containing sulfates, carbonates and nitrates, pitting action has been observed at the water-line, and also at the bottom of the tank.[59] Laboratory studies in which zinc was partially immersed in chloride solutions have shown that the metal is first immune at the water-line but corroded lower down, but that after a more extended period of exposure intense attack occurred at the water line.[60]

The explanation of this behavior,[61] which appears to account for water-line attack in galvanized cisterns as well, lies in the operation of a differential aeration cell. The area just beneath the surface of the solution, being more accessible to oxygen, becomes cathodic to the area lower down which, being anodic, begins to corrode. In the operation of this cell in the presence of alkali chlorides there is an accumulation of alkali in the aerated zone which, until it attains high concentration (corresponding to a high value for pH), results in the development of a protective film. It has been observed that water-line pitting becomes more pronounced in $2N$ and N potassium chloride than in 0.1 or $0.01N$ solutions.[58] Obviously, higher chloride concentrations permit the production of higher concentrations of alkali with greater probability of destruction of the protective film and pitting action.

In the water-line pitting of chloride-bearing waters it is possible that other constituents which are film-forming, such as carbonates and sulfates, if present in only moderate concentrations, contribute to pitting by providing a film of corrosion products which is discontinuous in character.

Effect of Impurities upon Corrosion of Zinc in Acids

The presence in zinc or zinc coatings of any metallic impurity which discharges hydrogen more readily than does zinc itself would be expected to increase corrodibility. It has been observed that antimony, copper and iron, which fall in this class, do accelerate the corrosion of zinc in dilute

[58] Borgmann, C. W., and Evans, U. R., *Trans. Electrochem. Soc.*, **65**, 257 (1934).

[59] Richards, H. F., *Iron and Steel Inst.*, **1**, 183 (1928).

[60] Bengough, G. D., and Wormwell, F., *Proc. Roy. Soc., London*, **A 140**, 402 (1933).

[61] For an excellent discussion of the mechanism of water-line corrosion see *Evans, J. Soc. Chem. Ind.*, **55**, 210 (1936).

sulfuric acid.[62] Lead and cadmium, unless present in more than the usual amount, have a negligible effect.[63] Indeed these elements have been shown to reduce the accelerating effect of antimony.[64] Small amounts of aluminum do not affect the corrosion of zinc in acid solutions.[65]

High purity zinc containing less than 0.0001 per cent of impurities is very resistant to attack by hydrochloric and sulfuric acids but corrodes readily in nitric acid.[66] Apparently nitric acid provides cathodic areas, probably a species of oxygen electrode on the pure zinc surface, which enables the metal to realize its natural tendency to corrode.

Performance of Zinc Coatings in Soils

Zinc coatings are commonly employed for the protection of steel anchor rods, culverts and similar structures against corrosion. In these cases a considerable proportion of the metallic surface is exposed to soils. Experience has shown that zinc coatings furnish considerable protection to ferrous metals in many soils, the exceptions being highly alkaline soils of a high chloride content and highly acid soils. In the former soils serious corrosion of galvanized anchor rods often occurs near the ground-line, a behavior suggestive of the water-line attack which sometimes occurs inside galvanized cisterns and has just been described.

Probably no environment in which metals are used is more complex and more varied than that provided by soils. Soils consist of a great variety of complex silicates and mineral residues ranging in particle size from colloidal clay to sand and gravel. They contain free and adsorbed salts, acids or bases and an admixture of organic matter. Soil structures are more or less permeable to moisture and air. At intervals following rains, water dissolves soluble constituents and seeps away at a rate which depends upon the texture of the soil and the slope of the terrain. Soils possess atmospheres which contain somewhat less oxygen but more carbon dioxide than the air above ground. There may be present also hydrogen sulfide, organic acid vapors, methane and various decomposition products of organic matter. Soil microörganisms and fungi are always present and these may influence acidity or the reducing or oxidizing nature of the environment.

Metals buried in soils are subject, then, to a most heterogeneous set of conditions which may vary from time to time depending upon the weather and other circumstances. Physical contact with soil particles is sometimes a factor in the production of corrosion cells of the differential aeration type.[67]

The most extensive and systematic test of the corrodibility of metals in soils is that sponsored by the National Bureau of Standards in 1922 and carried on over a period of more than twelve years. Originally this test was primarily designed to investigate the corrodibility of ferrous pipes in soil in the absence of stray electrical currents. It was later expanded to test approximately 9000 non-ferrous specimens including zinc and zinc-coated iron and steel. Something like ninety different soils were employed in this program of tests, although not all the metallic materials were buried in all of the soils.[68]

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[62] Vondrácek, R., and Izák-Krizko, J., *Rec. trav. chim.*, 44, 376 (1925).

[63] Prost, E., *Bull. Soc. chim. Belg.*, 28, 94 (1914).

[64] Patterson, W. S., *J. Soc. Chem. Ind.*, 45, 325T (1926).

[65] Harris, F. W., *Trans. Electrochem. Soc.*, 57, 313 (1930).

[66] Cyr, H. M., *Trans. Amer. Electrochem. Soc.*, 52, 349 (1926).

[67] Burns, R. M., and Salley, D. J., *Ind. Eng. Chem.*, 22, 293 (1930).

The rates of loss of weight and depth of penetration observed after ten years of burial of specimens of sheet and cast zinc in five soils is given in Table 9.[69]

Table 9.—Rates of Loss of Weight and Depth of Penetration of Zinc Buried Approximately 10 Years.[69]

	Soil 13		Soil 29		Soil 42		Soil 43		Soil 45	
	Loss	Pits	Loss	Pits	Loss	Pits	Loss	Pits	Loss	Pits
Sheet Zinc (99.5%)	0.35	4.0	0.46	3.9	0.085	1.7	0.23	3.3	f	f
Cast Zinc (99.5%)	.34	7.0	.53	5.5	.078	1.8	.22	6.8	0.94	9.8
Sheet Zinc (Standard)	.19	5.2	.38	f	.11	2.0	.45	3.7	f	f

Note: Loss of weight is expressed in ounces per square foot per year, and maximum penetration in mils per year. f = failure of one or more holes. Dimensions of sheet stock was 6 × 2 × 0.06 inches and cast stock 6 × 2 × 0.25 inches. Composition of material designated as "standard" is unknown but probably less pure than the other specimens of known composition.

The characteristics of these soils are given in Table 10.[70] It will be observed that the rate of corrosion of zinc in the alkali soils (Soils 13 and 45) and the acid muck (Soil 29) is the most severe, the tidal marsh (Soil 43) being next in order. These soils are also very corrosive toward ferrous materials. The remaining soil, (Soil 42), although markedly acid, is probably more representative of the average soil in regions of high rainfall and the results from this location show up very favorably for zinc. The average loss of weight of ferrous specimens at this location was approximately tenfold greater, and rate of pitting fivefold greater than for zinc during the same period.[71]

A more accurate idea of the protection afforded by zinc coatings against soil attack may be obtained from the results reported for the behavior of galvanized pipe and sheet included in the Bureau of Standards test of specimens buried in 1924. The coated pipes were 17 inches long and from 1½ to 3 inches in diameter, and the sheets were mostly 16-gauge metal 6 inches wide and 12 inches long. Most of the specimens carried 2-ounce coatings of zinc applied by the hot-dip process. The ferrous base materials employed were open-hearth iron pipe and sheet, Bessemer steel sheet and

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[68] Logan, K. H., Ewing, S., and Yeomans, C. D., *Bureau of Standards Technologic Paper No. 368* (1928).

[69] Logan, K. H., *Bur. Standards J. Research*, 17, 781 (1936).

[70] Compiled from data given in reference 69.

[71] Logan, K. H., and Taylor, R. H., *Bur. Standards J. Research*, 12, 119 (1934).

Table 10.—Properties of Soils in National Bureau of Standards Soil Corrosion Test of Zinc and Zinc Coatings.[70]

Soil No.	Soil Type	Location	Mean Temperature (° F.)	Annual Precipitation (inches)	Drainage of Test Site	Moisture Equivalent (%)	pH	Total Acidity Mg-eq. per 100 g. of Soils	Resistivity at 60° F. (ohm-cm.)	Composition of Water Extract mg-eq. per 100g. soil						
										Na+K as Na	Ca	Mg	CO_3	HCO_3	Cl	SO_4
1	Allis silt loam	Ohio	49.2	33.8	P	26.6	7.0	11.4	1215	0.72	0.25	0.43	0.00	0.09	0.09	0.83
3	Cecil clay loam	Ga.	61.2	48.3	G	29.1	5.2	11.5	30000	...	...	...	...	...	...	...
8	Fargo clay loam	N. Dak.	39.0	21.0	P	37.0	7.6	A	350	1.42	1.72	2.55	0.00	0.71	.01	4.43
11	Hagerstown loam	Md.	55.4	42.6	G	32.0	5.3	10.8	11000	...	...	...	...	...	...	...
13	Hanford fine sandy loam	Calif.	64.6	5.6	F	21.7	9.5	A	290	6.23	.09	.13	0.00	1.12	1.64	3.76
14	Hempstead silt loam	Minn.	44.2	27.2	F	17.2	6.2	5.6	3520	...	...	...	...	...	...	...
16	Kalmia fine sandy loam	Ala.	67.3	61.6	F	22.2	4.4	11.8	8290	...	...	...	...	...	...	...
18	Knox silt loam	Neb.	50.6	27.8	G	28.4	7.3	1.4	1410	.27	.63	.20	0.00	.94	0.00	.25
19	Lindley silt loam	Iowa	49.5	32.0	G	28.4	4.6	10.9	1970	.38	.32	.41	0.00	.16	.03	.46
20	Mahoning silt loam	Ohio	49.2	33.8	P	22.4	7.5	1.5	2870	.25	.48	.20	0.00	.51	0.00	.15
22	Memphis silt loam	Tenn.	61.6	47.7	G	28.4	4.9	9.7	5150	...	...	...	...	...	...	...
23	Merced silt loam	Calif.	65.0	6.0	P	24.7	9.4	A	278	8.38	.38	.22	.02	1.87	1.12	5.57
28	Montezuma clay adobe	Calif.	61.0	10.3	P	24.6	6.8	C	408	1.50	.06	.18	.00	.12	.99	.89
29	Muck	La.	69.3	57.4	VP	34.5	4.2	28.1	1270	2.15	1.92	1.55	.00	.00	1.69	2.30
32	Ontario loam	N.Y.	47.6	32.8	G	17.8	7.3	0.5	5700	.23	.70	.12	.00	.73	.01	.42
33	Peat	Wis.	46.1	30.1	VP	72.8	6.8	36.0	800	1.52	7.30	4.06	.00	C	2.27	2.13
37	St. John's fine sand	Fla.	69.3	47.4	P	7.0	3.8	15.3	11200	...	...	...	...	...	...	...
39	Sassafras silt loam	Del.	54.0	40.0	P	24.2	5.6	6.6	7440	...	...	...	...	...	...	...
40	Sharkey clay	La.	69.3	57.4	P	33.0	6.0	9.4	970	.56	.58	.44	.00	.93	.07	.28
42	Susquehanna clay	Miss.	64.0	53.0	P	34.8	4.7	28.2	13700	...	...	...	...	...	...	...
43	Tidal marsh	N. J.	52.0	43.0	VP	55.4	3.1	36.8	60	45.10	5.17	9.45	.00	.00	43.30	37.00
45	Alkali soil	Wyo.	47.2	15.3	P	14.8	7.4	A	263	8.15	3.70	.70	.00	.24	.18	11.98
46	Sandy loam	Colo.	50.0	14.1	G	7.6	7.0	C	1500	...	...	...	...	...	...	...

Notes: A = Alkaline; C = Not determined; G = Good; Mg-eq = milligram equivalent; F = Fair; P = Poor; VP = Very poor.

open-hearth steel containing 0.2 per cent copper. The results obtained at the end of approximately eight years in 23 soils are recorded in Table 11.[71] The properties of these soils are given in Table 10. Later results after burial for about 10 years in 43 soils are in substantial agreement with the results given in Table 11.[71a]

Table 11.—Corrosion of Galvanized Pipe and 16-Gauge Sheet.

Soil No.[1]	Duration of test (years)	Rate of loss of weight in ounces per square foot per year				Rates of penetration in mils per year[6]				Condition[7]			
		A (pipe)[2]	A3[3]	B[4]	Y3[5]	A	A3	B	Y3	A	A3	B	Y3
1	8.62	0.332	0.350	0.396	0.403	....	1.28	1.97	2.09	U	P	U	U
3	8.13	.038	.035	.034	.030	....	.74	.62	.62	E	R	R	E
8	8.73	.057	.033	.032	.035	....	....	....	....	E	E	E	E
11	8.66	.048	.029	.051	.047	....	2.42	2.89	3.23	R	P	P	P
13	8.25	.140	.207	.080	.238	....	1.82	.61	1.82	E	P	R	U
14	8.76	.028	.014	.014	.015	....	....	....	....	E	E	E	E
16	8.06	.333	.106	.161	.095	....	1.61	1.74	1.61	E	U	P	P
18	8.60	.029	.016	.015	.021	....	....	....	....	E	E	E	E
19	8.59	.069	.028	.040	.034	....	....	1.05	....	E	E	R	R
20	8.62	.141	.146	.306	.104	....	1.97	2.78	.81	R	P	P	U
22	7.97	0.98	....	....	....	....	....	....	....	R	...	...	...
23	8.25	^{9}.945	.358	.260	.628	^{9}6.67	3.58	2.12	4.00	P	P	P	P
28	7.73	^{8}.177	.463	.082	.066	....	5.95	.91	.65	E	P	U	R
29	8.10	^{8}.484	.286	.554	.390	1.98	4.94	3.21	4.70	P	P	P	P
32	8.63	.037	.026	.020	.022	....	....	....	....	E	E	E	E
33	8.63	.171	.171	.213	.182	....	1.85	1.97	1.62	U	P	P	P
37	8.06	.233	.338	.396	....	....	2.61	2.23	....	R	P	P	P
39	8.51	....	.113	.156	.107	....	2.35	1.88	2.00	...	P	P	P
40	8.09	.073	....	....	....	....	....	....	....	E	...	...	...
42	8.08	^{8}.036	.028	.027	.029	....	....	....	....	E	E	R	E
43	8.63	^{8}.114	.068	.155	.100	....	.81	3.82	.58	E	U	P	U
45	8.70	^{8}.284	.057	.302	.078	....	1.03	4.95	.69	U	U	P	U
46	8.69	.048	.008	.005	.007	....	....	....	....	E	E	E	E

Notes:
1. See Table 10 for description of soils.
2. A = pure open-hearth pipe.* Coating = 2.82 oz./ft.^{2}
3. A3 = pure open-hearth iron sheet.** Coating = 1.98 oz./ft.^{2}
4. B = Bessemer steel sheet. Coating = 1.62 oz./ft.^{2}
5. Y3 = open-hearth steel sheet, 0.02 per cent copper. Coating = 2.15 oz./ft.^{2}
6. Maximum penetration obtained by averaging deepest pit on each side of sheet.
7. Symbols: U = Uniformly corroded.
   E = Excellent.
   R = Rusted.
   P = Pitted.
8. Average of 2 specimens.
9. Average of 3 specimens.

* For analysis see *Bur. Standards Tech. Paper* No. 368, p. 515.

** As is customary, the weight of coating given for the pipe samples is the weight of zinc on the outside of the pipe, whereas the weight given for the sheet is the total weight of zinc divided by the area on one side of the sheet. Hence a 2-oz. coating on pipe in this table is twice as thick as a 2-oz. coating on a sheet.

From an examination of the corrosion results it is apparent that there is no significant difference in the corrosion-resisting properties of the specimens which can be attributed to the character of the ferrous base material. There is some indication that the specimens with the lightest weight of coating (those designated as B groups) rusted somewhat more readily than the heavier coatings, a result which was obtained more conclusively in an additional test carried out in six of these soils over a period of six years using specimens of a wider range of coating thicknesses.

In general these studies have shown that zinc coatings provide considerable protection to iron and steel. A comparison of average rates of loss of weight of zinc-coated and bare ferrous specimens in these soils over a period of eight to ten years shows that the latter corrode 5.6 times more rapidly than do the zinc-coated specimens. This is based on the average rate of loss of weight of 0.148 ounce per square foot per year for all zinc-coated specimens in all soils, as against 0.840 ounce per square foot per year for all ferrous samples in the same soils.[71]

[71a] Logan, K. H., and Ewing, S. P., *J. Research, Nat. Bur. Standards*, **18**, 361 (1937); R P 982

An accurate correlation of rates of corrosion with soil characteristics is difficult owing to the different relative influence of the numerous and complex variables in soil exposures. From an inspection of the data of Table 11 it may be seen that the soils may be classified, with respect to corrosiveness toward zinc coatings, into three groups: mildly corrosive, moderately corrosive, and severely corrosive. In the first group exhibiting least attack are soils 3, 8, 11, 14, 18, 19, 32, 42 and 46. These soils, with the exception of 3, 11 and 42, are in areas of low rainfall and at sites where the drainage is good. All are of moderately high electrical resistivity and low salt content (where data are available) except soil number 8, which is low in resistivity and high in sulfates. The average loss in weight for all zinc-coated specimens in these soils was 0.030 ± 0.009 ounce per square foot per year, and the rate of penetration 1.50 ± 0.86 mils per year.

In the group of soils of intermediate corrosiveness toward zinc-coated specimens are soils 13, 16, 20, 28, 33, 39, 43 and 45. These were for the most part poorly drained and high in salt content. The average annual loss of weight for all specimens in these soils was 0.155 ± 0.03 ounce per square foot, and the average annual penetration 1.84 ± 0.2 mils.

The poorest performance of zinc coatings was in soils 1, 23 and 29. These were all poorly drained and of low resistivity. The first was neutral and of moderate salt content, but the second, soil 23, was highly alkaline and the third highly acid in character. Both 23 and 29 were high in alkali sulfates. The values for average annual loss in weight were 0.45 ± 0.07 ounce per square foot and the average annual penetration 3.16 ± 0.9 mils per year.

In view of the foregoing analysis of soil corrosion results it is possible to make rough estimates of the life of zinc coatings in soils representative of the three classes of corrosiveness. The life in a given soil or soil type appears to be proportional to the thickness of coating in much the same manner as in atmospheric exposure. Assuming that a reasonable criterion of the protective value of zinc coatings in soils is the period during which rusting is prevented over the major area of the ferrous metal surface, and allowing for about 20 per cent variation in thickness of coating, it is possible to make the following estimates of the life of zinc coatings of one ounce per square foot of surface area in soils of the three degrees of corrosiveness described above.

Corrosiveness of Soil	Life of Coating of 1 oz./ft.^{2}
High	1-2 years
Moderate	4-6 years
Mild	18-25 years

Protective Value of Zinc Coatings Against Corrosion Fatigue of Steels

Steels and many other metals when subjected under certain circumstances to repeated stresses may develop fatigue cracking. It became recognized a few years ago [72] that the nature of the environment affects the endurance of metals to such stressing, and the term, "corrosion-fatigue" was applied to the embrittlement and cracking which result from the simultaneous application of tensile and compressive stresses and corrosive media. The corrosion-fatigue limit of a metal is the highest stress which it will endure indefinitely (that is, for at least ten million cycles of stress), when subjected to repeated stresses and exposed simultaneously to a corrosive medium. Although air may be considered a corrosive medium, since in some cases at least its exclusion leads to higher corrosive-fatigue values,[73] most studies of corrosion-fatigue have been conducted in water and aqueous solutions.

The observation that the corrosion-fatigue limit of a steel exposed to salt water is lower than that of a steel exposed to fresh water containing a high content of carbonate led to the conclusion that the film-forming characteristics of the latter were related to the result. A somewhat similar improvement in corrosion-fatigue resistance was obtained by the introduction of chromium, a film-forming substance, into steel. In view of these results the use of protective metallic coatings for the prevention of corrosion-fatigue suggested itself. Tests employing cadmium coatings were favorable, and these led to a study of the protective value of zinc coatings for this purpose.

Zinc coatings were applied to a fairly hard steel in the form of round rods by hot-dipping, sherardizing and electroplating, and these specimens were employed in a rotating beam type fatigue machine to investigate the protective action of zinc against the corrosion fatigue of steel in a moderately hard water.[74] The machine was operated at 1750 r.p.m., and the test carried out in a temperature range of 65 to 76° F. The results of the test on these specimens were as follows:

Material	Fatigue Limit (lbs./in.^{2})
Bare steel	20,000
Hot-dipped zinc coating	43,500
Sherardized zinc coating	43,500
Electroplated zinc coating	60,500

Toxic Properties of Zinc

There is some uncertainty concerning the toxic properties of zinc despite the fact that much has been written on the subject. Zinc is found normally in plant and animal tissues and is known to be excreted by the body. The conclusion seems warranted, however, that consumption of zinc beyond a small amount which may be necessary for the proper functioning of the animal system may give rise to toxic effects. The U. S. Public Health Service has placed a maximum safe limit on the zinc content for culinary and drinking water supplied by common carriers at 5 milligrams per liter.[75] This limit is considered conservative by other investigators [76] who, from a review of the literature and their own experiments, conclude that 40 milligrams of zinc per liter of water is safe for human consumption. It has been pointed out, for example, that water from galvanized storage tanks containing 17.1 parts per million supplied for drinking purposes at Brisbane, Australia, caused no observably harmful results.

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[72] McAdam, D. J. Jr., *Pro. Am. Soc. Testing Materials*, **26**, Pt. 2, 224 (1926).

[73] Gough, H. J., and Sopwith, D. G., *J. Inst. Metals*, **56**, 55 (1935).

[74] Harvey, W. E., *Metals and Alloys*, **1**, 458 (1929-30).

The zinc content of ground waters flowing through galvanized pipe is commonly from 5 to 15 parts per million.[77] As previously stated in this chapter, soft waters and waters containing carbon dioxide attack zinc more rapidly than do hard waters. The percentage of zinc actually present in tap water in any given case depends also, of course, upon the length of the galvanized section through which it has passed and the length of time it has stood in this pipe.

It has been contended that chlorination of water increases its corrosiveness toward zinc.[78] Recent studies have shown, however, that water containing 5 parts per million of chlorine produces less attack on galvanized iron than does distilled water.[76]

It is generally recognized that zinc-coated dishes are unsuitable for use in the preparation of foods, particularly acid foods. The use of zinc-coated containers, pails, tubs and the like in making lemonade and similar drinks, which used to be not infrequent for large gatherings, is especially to be guarded against. An investigation by the Bureau of Chemistry of root beer which was suspected of being the cause of numerous cases of slight poisoning indicated that the beverage contained 229 milligrams of zinc per liter. Tests made to show the rate at which various liquids would dissolve zinc when allowed to stand in a zinc-coated pail gave the results summarized in Table 12.[79]

Table 12.—Zinc Dissolved from Zinc-Coated Iron Pails.

Liquid	Zinc, mg/liter after 17 hours	Zinc, mg/liter after 41 hours
Tap Water (Washington, D. C.)	5	21
Distilled Water	9	27
Carbonated Water	193	181
Milk	483	1054
Orangeade	540	854
Lemonade	1411	2700

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[75] U. S. Public Health Service Reprint 1029, page 693, Public Health Reports, April 10, 1925.

[76] Anderson, E. A., Reinhard, C. E., and Hammel, W. D., *J. Am. Water Works Assoc.*, **26**, 49 (1934).

[77] Howard, C. D., *J. Am. Water Works Assoc.*, **10**, 411 (1923).

[78] Lothian and Ward, *J. Roy. Army Med. Corps*, **39**, 169 (1922).

[79] Sale, J. W., and Badger, C. H., *J. Ind. and Eng. Chem.*, **16**, 164 (1924).

Chapter 7

Cadmium Coatings and Their Protective Value

The importance assumed by cadmium coatings in recent years may be attributed to the pleasing appearance of the metal and the fact that, indoors at least, it furnishes satisfactory protection against rusting. Although somewhat similar to zinc in its properties, cadmium darkens less readily and usually does not develop corrosion products of a bulky and loose nature. Owing to the high cost of cadmium which has increased in recent years, it has not attained very widespread use. Since, as will be shown later, its efficacy as a protective coating is in general inferior to that of zinc, interest in cadmium as a coating material has waned of late. In actual volume of plating, however, cadmium coatings increased over the period 1929 to 1936 largely as a result of its adoption for certain applications such as electrical contacts, radio apparatus, washing machines, etc.[1]

Cadmium, like zinc, is electronegative or anodic to iron and protects exposed areas of an iron surface by sacrificing itself.[2] The potential difference between cadmium and iron is less than that between zinc and iron, and for this reason cadmium does not in general cathodically protect as large an area of exposed iron as does zinc. Indeed it is possible that in some environments the potentials of cadmium and iron may be reversed, permitting "pinhole" corrosion of iron through pores in the cadmium coating.

METHOD OF APPLICATION OF CADMIUM COATINGS

Cadmium coatings are applied on a commercial scale only by electroplating. Some effort has been made to produce coatings by hot dipping [3] and also by metal spraying, but neither method has attained much importance. Sprayed cadmium coatings are said to be used abroad, however, on propeller shafts, Diesel engine walls and buoys in contact with sea water.[4] The first patent on the electrodeposition of cadmium was issued in England in 1841; the process was in successful but limited operation shortly thereafter. Not until about fifteen years ago, however, was the metal electroplated on a commercial scale as a protective coating. It is of interest to note that the solution first used for cadmium plating—cadmium carbonate dissolved in a solution of sodium cyanide—is of the same general nature as those used in commercial cadmium plating at the present time.

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[1] Soderberg, K. G., *Monthly Rev. Am. Electroplaters Soc.*, 23, 33 (Nov., 1936).

[2] Rawdon, H. S., *Trans. Am. Electrochem. Soc.*, 49, 339 (1926).

[3] Siemens, A., *Met. Ind. (London)*, 36, 481 (1930); *see also*, DeLattre, *Rev. met.*, 25, 630 (1928).

[4] Humann, *Werft, Ruderer and Hafen*, 16, 40 (1935).

Modern cadmium plating solutions are prepared by dissolving cadmium cyanide or cadmium oxide in sodium cyanide, obtaining the double cyanide of cadmium and sodium, $NaCd(CN)_3$ and usually some "free cyanide." The cadmium content of the bath may vary from 0.25 to 0.8*N*, *i.e.*, from 15 to 30 grams per liter, and the free sodium cyanide from 0.15 to 0.6*N*, *i.e.*, from 7.5 to 30 grams per liter.[5] A typical cadmium plating bath may contain 0.35*N* CdO (23 grams per liter), 1.5*N* sodium cyanide (75 grams per liter), and 0.4*N* sodium hydroxide (15 grams per liter). Addition agents, for example, gulac, which is a waste product of the sulfite pulp industry, may be employed to improve the character of deposit.[6] The use of a very small percentage of nickel in the cadmium bath produces a bright deposit.[7]

The plating solution is operated at ordinary room temperature and in the current density range of 1 to 5 amperes per square decimeter (9 to 47 amperes per sq. ft.)[5] Cadmium anodes may be successfully used. Owing to the tendency in some baths toward anode corrosion it has been recommended that stainless steel be used to replace up to 75 per cent of the anode area.[8]

Cadmium plating baths contain the complex cadmium-cyanide radical $[Cd(CN)_3]^-$ an analog of the complex zinc ion $[Zn(CN)_4]^{--}$. As in the case of cyanide-zinc solutions, the cadmium cyanide bath, owing to the low degree of dissociation of this complex ion, maintains a very low metal ion concentration, and consequently has a high throwing power. It is well known that cadmium baths produce coatings of a good degree of uniformity on parts of irregular shape.

Zinc-cadmium alloys may be readily deposited from cyanide solutions containing the two metals. It is usually difficult to control the composition of the deposit, the variation in cadmium content running from about 4.5 to 15 per cent. These alloy coatings are initially somewhat brighter than zinc in appearance, but become mottled and unsightly upon short exposure out of doors.[9]

Protective Value of Cadmium Coatings

There was for several years considerable controversy as to the value of cadmium coatings for the protection of iron and steel and particularly as to their relative efficacy as compared with zinc coatings.[10] Much of the interest in cadmium coatings arose from their favorable showing in the salt spray test at a time when greater credence was given to the dependability and significance of accelerated tests. With the decline of faith in accelerated testing it continued to be argued that the salt spray test in simulating marine atmospheres gives a reliable estimation of the relative behavior of materials to be used in seaside localities and aboard ocean-going ships. While there is some merit in this contention, more recent atmospheric exposure tests have shown that even in marine locations cadmium is inferior to zinc. Cadmium does, however, resist attack in these locations markedly better than it does in industrial atmospheres. Contrary to the behavior of zinc coatings it is found that cadmium plate is somewhat more severely attacked in a marine exposure in the tropical zone than in a similar location in the temperate zone.

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[5] Blum and Hogaboom, "Principles of Electroplating and Electroforming," 2nd ed., p. 334, New York, McGraw-Hill Book Co., 1930.

[6] Blum, W., Strausser, P. W. C., and Brenner, A., *Bur. Standards J. Res.* 16, 185 (1936).

[7] Westbrook, L. *Trans. Am. Electrochem. Soc.* 55, 333 (1929).

[8] Wernick S., *Trans. Electrochem. Soc.*, 60, 117 (1931).

[9] Hippensteel, C. L., and Borgmann, C., *Trans. Am. Electrochem. Soc.*, 58, 23 (1930).

[10] Gillett, H. W., *Metals and Alloys*, 1, 667 (1929-30).

The joint atmospheric corrosion test on electroplated coatings being conducted through the coöperation of the American Electroplaters' Society and the American Society for Testing Materials with the National Bureau of Standards has included a study of cadmium coatings.[6] This test has been mentioned previously and the results obtained for zinc coatings are given in Table 7 in Chapter 6. The results obtained for cadmium coatings in this test at the end of an exposure of about 180 weeks are given in Table 13. It will be recalled that a system of rating quality, in which more importance was attached to the early stages of rusting, was devised for

Table 13.—Quality Ratings and Per Cent of Surface Rusted for Cadmium Coatings. 180 Weeks' Exposure to Atmosphere.[6]

Description of Plating Bath	Thickness mils (in.×10³)	New York T %	New York R %	Pittsburgh T %	Pittsburgh R %	Sandy Hook T %	Sandy Hook R %	Key West T %	Key West R %	State College T %	State College R %	Washington T %	Washington R %
Standard	0.2	16	75	17	75	43	75	81	..	94	4	59	75
Cyanide	.5	26	75	43	75	94	3	81	..	100	0	97	3
	1.0	44	75	81	65	94	0	81	..	100	1	96	2
Cyanide with gulac.	.2	16	75	17	75	47	75	81	..	85	8	58	75
	.5	27	75	37	75	88	3	81	..	100	0	97	2
	1.0	46	75	71	75	96	0	81	..	100	0	100	0
Cyanide with gulac. and nickel	.2	14	75	18	75	46	75	81	..	87	8	78	75
	.5	28	75	34	75	90	6	82	..	100	0	96	2
	1.0	44	75	81	75	97	0	82	..	100	0	99	1

evaluation of the results. This quality rating over the period of test is expressed in the table as (T), and per cent of surface rusted at the end of the test as (R).

Comparison of the results in this table with those recorded in Table 7 for coatings of zinc exposed at the same test stations shows that without a single exception the quality ratings of the cadmium coatings are lower than those for zinc coatings of similar thickness. The comparison shows further, as stated above, that the superiority of zinc coatings is somewhat less pronounced in marine locations than in industrial, urban and rural exposures.

Cadmium and zinc coatings have been compared in performance in the extensive atmospheric exposure program of tests being carried out by the American Society for Testing Materials. The comparative behavior of the two coatings plated on steel plates and zinc-dipped corrugated sheets obtained in this test over a period of nine years at Brunot Island, Pittsburgh is shown graphically in Figure 27.[11] The progressive development of rust on cadmium and zinc-coated hardware specimens for a shorter period at the same location is given in Figure 28.

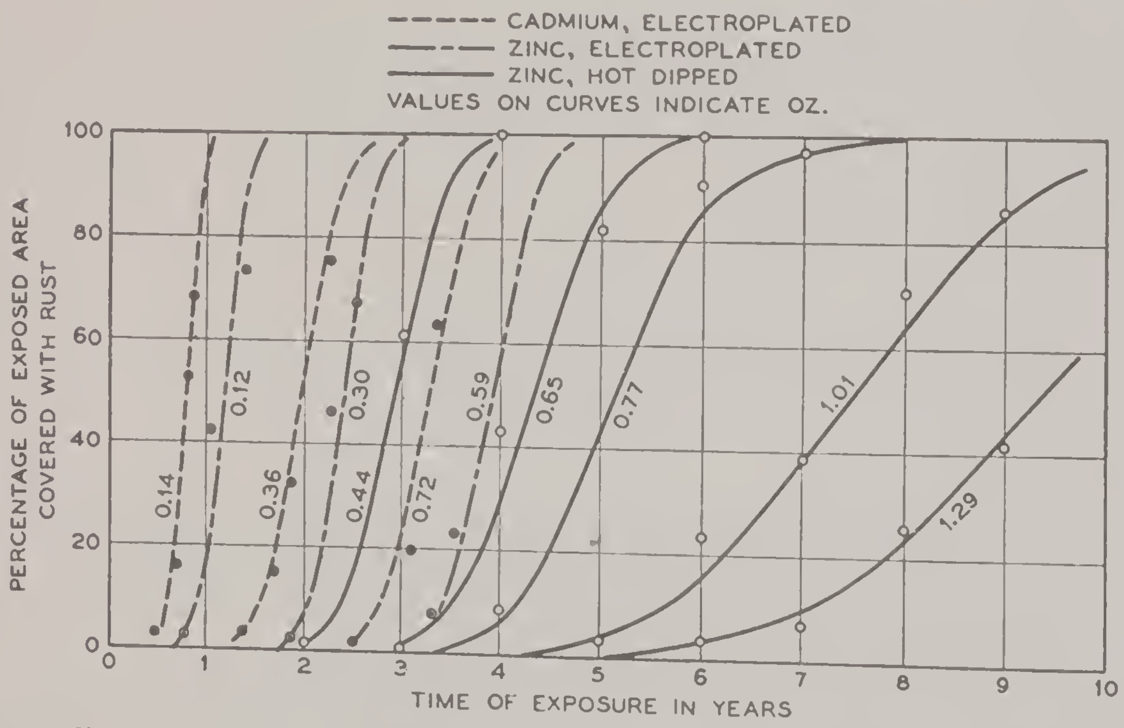

Figure 27.—Progressive Development of Rust at Brunot Island (Pittsburgh, Pa.) on 4- by 6-in. Steel Specimens Plated with Cadmium and Zinc and on Corrugated Galvanized Sheets.

These tests likewise demonstrate the marked inferiority of cadmium coatings in an industrial atmosphere. It is of interest to note that the protection afforded to steel by cadmium coatings is proportional to the thickness of the coating, as has been well established for zinc coatings.

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[11] Passano, R. F., *Proc. Am. Soc. Testing Materials*, 36, pt. I, 107 (1936).

The more rapid corrosion of zinc coatings in industrial atmospheres has been attributed to their inability to develop, in such exposures, films of corrosion products which are basic in character and of low solubility. It would appear from the behavior of cadmium coatings in similar atmospheres that the surface films must be of even higher solubility than in the case of zinc. While the composition of corrosion products is usually complex and variable, those forming in industrial atmospheres generally contain sulfates, and it may be significant in this connection that cadmium sulfate is nearly twice as soluble as zinc sulfate. It is generally recognized that the lower solubility of cadmium chloride as compared with zinc chloride accounts for the greater resistance of cadmium coatings in the salt spray test. Inasmuch as this superiority of cadmium in salt spray is not realized in outdoor marine exposures it is evident that the corrosion products formed in such localities are probably not merely the chlorides of the metals.

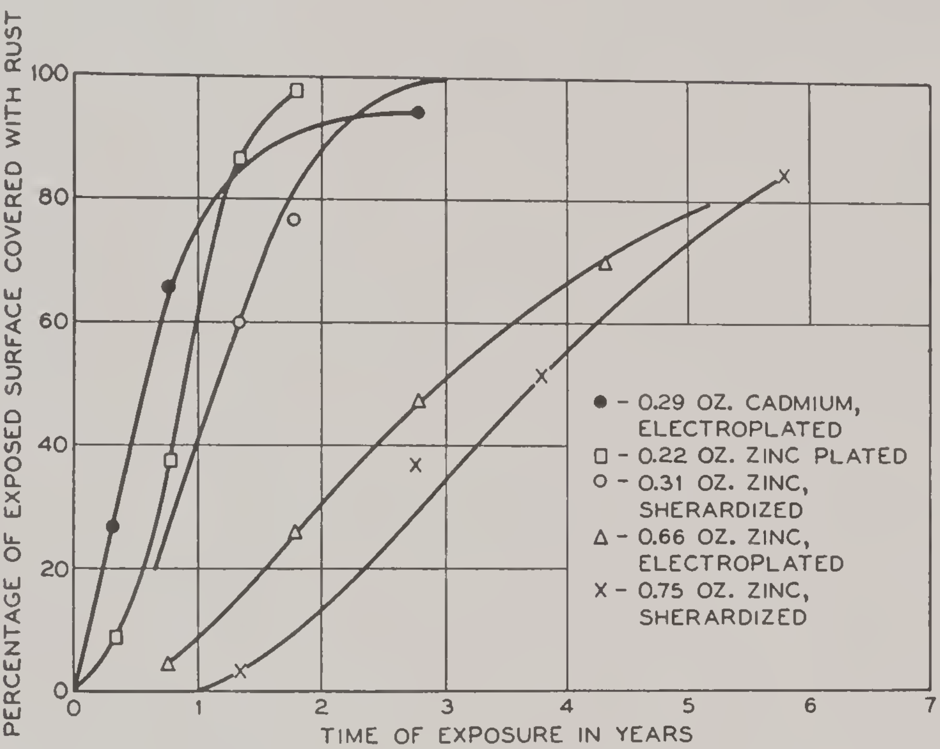

Figure 28.—Progressive Development of Rust at Brunot Island (Pittsburgh, Pa.) on Hardware Specimens Coated with Zinc and Cadmium.

The effect of spraying cadmium coatings with water, thereby simulating increased rainfall, does not increase the rate of corrosion of cadmium in New York City atmosphere. See Figure 22 in Chapter 6 for a comparison of zinc and cadmium coatings as influenced by water spraying. Apparently the natural rainfall which occurs at this test station is sufficient for the dissolution of the cadmium corrosion products, but inadequate for the removal of the film forming on zinc.

The favorable performance of cadmium coatings in indoor service may be attributed to the fact that in air of moderate humidity films of protective character tend to form. For example, it has been observed that cadmium coatings under such conditions gain weight with time of exposure in accordance with a roughly parabolic law.[12] This suggests that the progress of the reaction is controlled by the rate of diffusion of oxygen or other corroding elements through the increasingly thicker film of corrosion products. In contrast to this it will be recalled that the film formed on zinc under such conditions is of such nature as not to retard corrosion.

Under conditions of higher humidity indoors the corrosion products of cadmium coatings become deliquescent, with the result that the rate of attack is accelerated. There is evidence that the relative humidity at which cadmium corrosion products become deliquescent is markedly lower than it is for the corrosion products of zinc.[12] This tendency of cadmium to develop a film of moist material on its surface at relative humidities well below the dew point may be a factor accelerating the corrosion of cadmium coatings outdoors.

Finally it may be of interest to note that the relative rates of corrosion of cadmium and zinc are of the same general order as their equivalent weights, 56 and 33 respectively.

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[12] Patterson, W. S., *J. Electroplaters and Depositors Tech. Soc.*, 5, 91 (1930).

Chapter 8

Tin Coatings

Tin-plate combines in a single material the relatively superior corrosion resistance of a non-ferrous metal with the strength of steel. Tinned sheet metal can be severely deformed without serious damage to the coating; consequently rather complicated articles are produced by stamping, drawing, rolling, bending, curling, and lock-seaming. Tin is in many respects an excellent coating metal. It can be applied as an extremely thin and reasonably uniform coating over the surface and is resistant to atmospheric corrosive attack and to aqueous solutions in the absence of oxygen. Since tin lends itself admirably to soldering operations and has no toxic effect upon foodstuffs in contact with it, tin-plate is used in great quantities in the canning industry. Indeed it may be said that the canning industry, which is so important a feature of modern life, is based upon the suitability of tin-plate as containers for the preservation of foods. In 1935 approximately 59 per cent of the domestic consumption of tin-plate was used in canning, all other applications using but 41 per cent of the million and a half tons of tin-plate consumed in this country in that year.[1]

The annual world consumption of tin-plate would be sufficient to supply a band of this material 100 feet wide and long enough to girdle the earth at the equator, and the tin used annually in solders (if alloyed with 50 per cent lead) would provide 250 soldered seams to parallel this equatorial band.[2] About 40 per cent of the world production of tin goes into tin-plate.

In addition to its use in the form of tin-plate, tin is employed to a much lesser extent in coating copper. Among the applications of tinned copper are roofing material, cooking utensils and refrigeration equipment. In the electrical industry tinned copper wire is used in considerable quantity.

Tin coatings have been applied almost exclusively by hot-dipping until recently, and the term "tin-plate" for tin-coated steel has been associated with the dipping process. In recent years electrodeposited coatings have assumed greater importance and this trend may be expected to continue, owing to the development of processes for continuous electroplating of steel strip. The application of tin coatings by wiping fused tin over the surface to be coated is restricted to copper. Tin coatings may be applied readily by the metal-spraying process. By spraying thick coatings or by scratch-brushing successive layers of sprayed tin the porosity characteristic of this type of coating may be diminished. Recently it has been shown that tin coatings may be deposited from the vapor phase by decomposition of stannous chloride vapor in a hydrogen atmosphere.[3] This process which has been called "stannising," has been applied so far only in an experimental way and principally to copper. The coating consists of an alloy of tin and the basis metal.

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[1] Statistical Yearbook (1937) *Internat. Tin Research and Dev. Council.*

[2] Macnaughton, D. J., *Address,* Amer. Inst. Min. and Met. Eng., New York, Feb. 21, 1935. Published by International Tin Research and Development Council, No. 5, October, 1935.

HOT-DIPPED TIN COATINGS

Historical

Metallic tin has been used for many centuries. As early as 1500 B. C. the Phoenicians were obtaining tin from Cornwall for use in making bronze. The coating of copper vessels with tin was known to the Romans as was the tinning of cast-iron cooking utensils which were mentioned by Pliny as existing before 23 A. D.[4] There is evidence[5] that the coatings were applied by immersion in a bath of molten tin. It is reasonable to believe, however, that the much simpler process of tinning by applying the metal to the surface of the heated article was also employed by the ancients.

Coating sheet iron with tin is of much more recent origin. According to legend a Cornish tin miner discovered tin in the Erzgebirge mountains of Bohemia about 1240 A. D.[6] The tin-plate industry seems to have become well established in Bohemia between this date and 1575 A. D. when it is recorded that block tin was imported from Cornwall for the manufacture of tin-plate, the local supply apparently being insufficient to meet the increasing demand. About 1600 the manufacture of tinned iron sheets was begun in Saxony, and by 1665 Dresden had become a flourishing center for the production of this material. It is said that the secret of the art was stolen for the Duke of Saxony by a monk who visited Bohemia in disguise.

The introduction of tin-plate manufacturing into England was the result of the efforts of Andrew Yarranton who, during a depression of the metal industry in England, particularly relating to tin and iron, visited Dresden for the express purpose of becoming familiar with the manufacture of tinplate. Accompanying Yarranton, according to his well-known book, *England's Improvement by Sea and Land,* was a man "that well understood the whole nature of iron." The party was well received in Dresden and no efforts were made to conceal any of the operations. Upon returning to England with the information sought, Yarranton made preparations for starting the industry at Pontypool in southwestern England. The establishment of the industry was a slow process, for although Yarranton applied himself to "setting this beneficial thing to work" his efforts failed owing to the granting of a patent for the process to a rival who had influence at court. In 1697 Houghton reported that there were no tin-plate works in Great Britain. Not until 1720 when Hanbury took up the project again at Pontypool was the tin-plate industry in England definitely established. Once started, the industry grew rapidly, especially after a method for producing the iron sheets by rolling instead of hammering them by hand was developed in 1728. The South Wales district became the center for the production of practically all of the world's supply of tin-plate, a position which it retained until late in the 19th century. The abundance of iron ore, wood for charcoal and the discovery of pit coal in 1870 made this region a particularly favorable one for the industry.

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[3] Gonser, B. W., and Slowter, E. E., *Internat. Tin Research and Dev. Council, Tech. Pub. (A)* No. 76, April, 1938.

[4] Flower, P. W., "History of Tin and Tin-Plate," London, G. Bell & Sons, 1880; *J. Iron Steel Inst.*, No. 1, p. 36 (1886).

[5] Goodale, "Chronology of Iron and Steel," Pittsburgh Iron and Steel Foundries Co., 1920.

[6] Macnaughton, D. J., and Hedges, E. S., *Internat. Tin, Res. and Dev. Council*, Bull. No. 1, Feb., 1935. This bulletin has been drawn upon for historical aspects of the tin-plate industry.

The manufacture of tin-plate in the United States was begun about 1891 following the enactment of the McKinley tariff which imposed a duty of 2.2 cents per pound on tin-plate. In recent years this country has become the largest producer of tin-plate, accounting in 1935 for 53.8 per cent of the world's output. There are 17 companies operating 28 plants with a total annual capacity of 2,574,000 long tons of tin-plate. Nearly 99 per cent of the tin-plate produced in the United States is of the type known as "coke" tin-plate containing approximately 35 pounds of tin per long ton of product, in contrast to the heavier coated variety known as "charcoal" tin-plate.

Outline of the Process

As in the analogous case of zinc coating, the application of a tin coating to a material such as steel sheet constitutes only a small part of the total work required in preparing such material. Although there are characteristic differences in preparing the sheets in the zinc coating and tin coating industries, the essentials are the same.

Following the introduction of rolling mill technique, iron sheet was used for tinning until about 1870 when it was gradually displaced by Bessemer steel. It was early found advantageous to roll the sheets in packs. This is accomplished by hot rolling bars of steel to the finished gauge by preheating, rolling, and doubling until a pack of eight sheets is produced uniform in substance and of correct gauge.[6] It is more common practice at present to cut the hot-rolled steel at an early stage into a large number of small bars which are then rolled to the final thickness. With the development of the process of continuous rolling of steel strip, the older methods of producing sheet stock for tin-plate are being superseded. In the United States, steel ingots weighing several tons are rolled to tin-plate gauge, producing strip which may be 5000 feet in length and 3 feet in width. While strip 10 inches in width is being tinned continuously on a commercial scale, the present practice is to cut the wider strip into relatively short lengths for the tinning operation.[7]

The hot-rolled sheets are carefully cleaned by acid pickling. This process is carried out in two stages: the first, which is termed "black pickling" is accomplished by immersing the black sheets in sulfuric acid (approximately 6- to 12-per cent) which is kept hot with steam. After the annealing, cold rolling and second annealing operations which follow the first pickling, the sheets are given the "white pickling" in dilute sulfuric acid (2- to 6-per cent), and after washing are ready for the tinning operation.

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[7] Macnaughton, D. J., Tait, W. H., and Bair, S., *J. Electrodepositors' Tech. Soc.*, 12, 45 (1937).

Hand Dipping

The old process for making tin-plate by hand dipping is of interest. The sheets were cleaned by scouring with sand and water and by being immersed in sour barley water for several days. The use of sulfuric acid for pickling dates only from the early part of the nineteenth century. The sheets, after being cleaned, were immersed in a bath of hot grease before immersion in the molten tin. Tallow, which was used in the early days and is used to a limited extent today in hand dipping, was replaced later by palm oil which is still widely used for this purpose. From the grease pot the sheets were lowered one by one into the molten tin which was kept covered with a thick layer of the grease in order to prevent oxidation. Upon removal from the first tin bath, the sheets were brushed with a hemp brush and immersed in a second tin bath usually of somewhat higher purity and maintained at a somewhat lower temperature than the first, and finally in a third tin bath of highest purity. Close regulation of the amount of tin carried by the sheet was not possible although the workmen became very adept in obtaining very uniform distribution of the coating over the surface of the sheet. After the coating had solidified, the sheets were rubbed free from most of the oil by means of bran or a similar substance and then "dusted" with a sheep fleece to give a high luster. Sheets coated in this manner always had a very heavy coating as compared with the present commercial "coke" plate.

The present hand-dipping method for tinning small irregularly shaped castings and for tinning articles cut or manufactured from tin-plate or plain "black" sheet steel, such as kitchen utensils, does not differ essentially from the old hand-dipping method. The retinning of articles is also done in essentially the same manner. Considerable difficulty is often experienced in tinning castings by hand dipping, primarily on account of an improperly cleaned surface. The first cleaning is often done with hydrofluoric acid, and sometimes sand blasting is employed. After this, the casting is pickled and the resulting film of graphite must then be carefully rubbed off. Following this, a treatment with a copper solution to give a film of precipitated copper is often recommended.[8] The article is then immersed in the molten tin, the flux commonly used being zinc chloride. Iron castings which have been given an annealing treatment somewhat akin to the treatment used for producing malleable castings, so that surface decarbonization has been brought about, can be tinned, as a rule, very much more readily than ordinary castings.

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[8] Schott, E. A., *Stahl Eisen*, 39, 119 (1919); *Marnoch, Giesserei*, 37, 691 (1926); *Iron Age*, 118, 1318 (1926).

Mechanical Dipping

A marked advance in the tinning process was the invention, about 1863, by Morewood and, independently, by Saunders and Piper, of a device for passing the sheets as they came from the bath through a set of rolls located in the oil layer above the tin. The rolls worked rather closely against each other so that the molten tin was distributed uniformly over the surface.

The use of zinc chloride as a flux for treating the sheets prior to immersion in the tin accompanied and, to some extent, made possible the use of the single bath of tin instead of the several separate baths used in the early days. The single-bath method is used today almost exclusively for tinning when carried out mechanically, although the bath is usually divided into two compartments. Figure 29 is a section of a tinning pot used early in the industry and shows the arrangement of the essential features, flux, molten tin bath, palm-oil layer and rolls. The sheets, after being cleaned, were fed by hand one at a time through the flux into the tin and then raised vertically by the lever so as to be caught by the rolls and carried upward and out of the pot. This method in principle is still used, though to a very

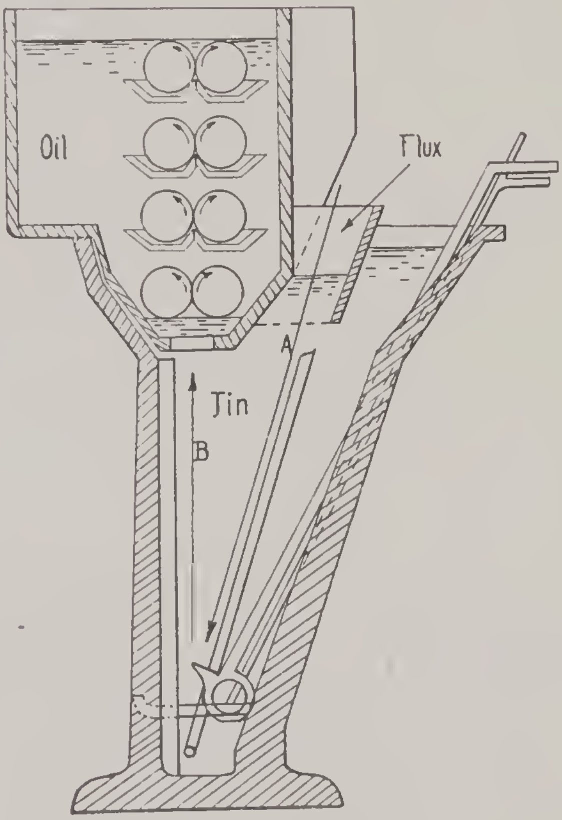

Figure 29.--Early Form of Tinning Machine. The arrows indicate how the sheet is passed through the tin and oil baths. The pans beneath the exit rolls contain molten tin to aid in forming uniform and heavy coatings. [Harbord, F. W., and Hall, J. W., "Metallurgy of Steel," 7th ed., Philadelphia, J. B. Lippincott Co., 1923.]

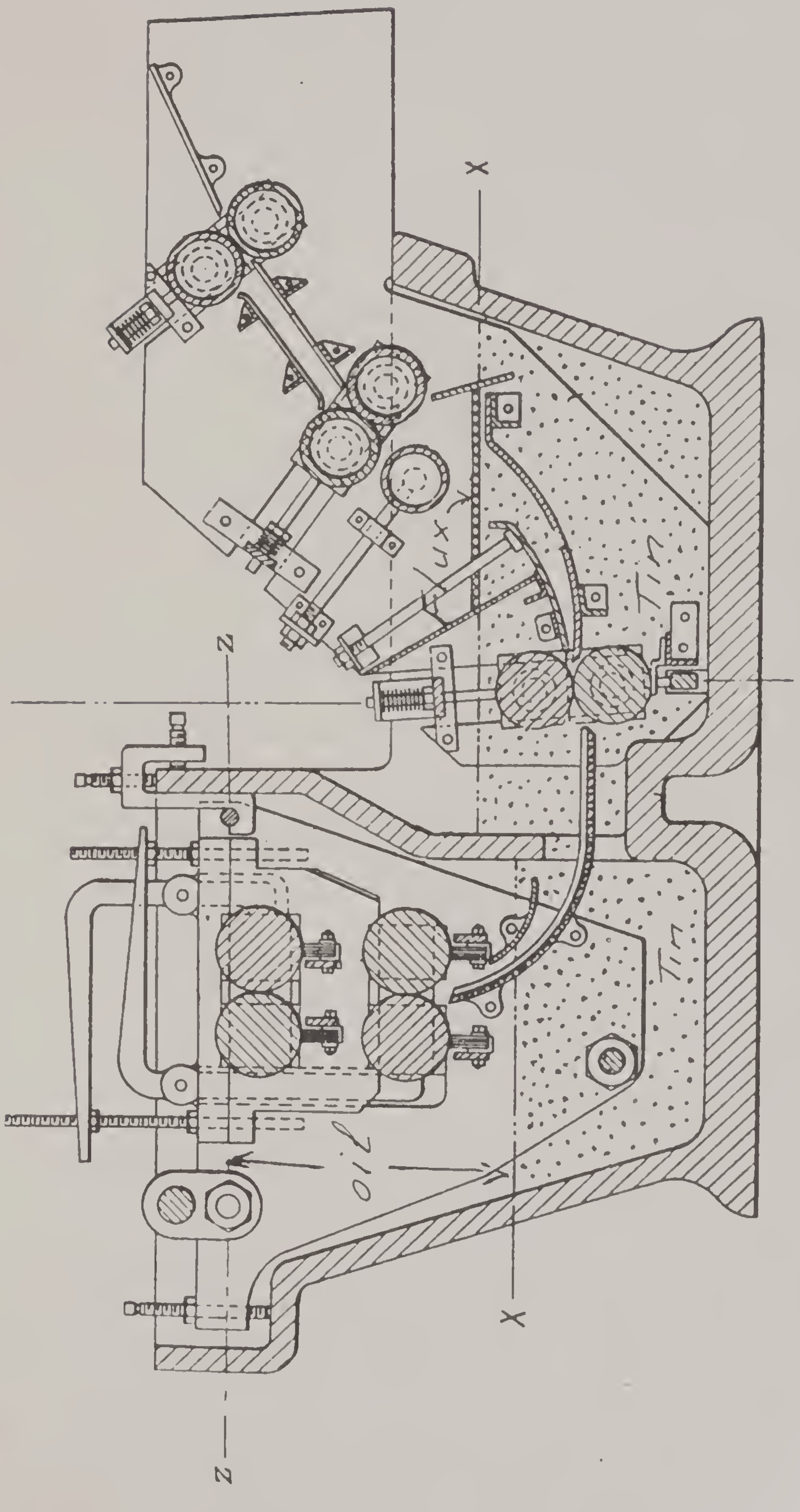

Figure 30.—Section of "Tin Pot" of a Modern Tinning Machine.[10]

limited extent,[9] for the production of heavily coated tin-plate. It is not suitable for very long sheets which are apt to buckle and bend when raised from the lower edge, nor is the method a rapid one.

Figure 30 shows a section of a tin pot in current use for the mechanical tinning of the grade of tin-plate commonly termed "coke-plate."[10] Such a pot contains from 5000 to 10,000 pounds of tin.

After being cleaned the sheets are passed through the zinc chloride flux layer into the molten tin by means of the rolls and guides at the right. The molten metal in the first compartment of the cast-iron container is generally kept at a somewhat higher temperature than that in the second. The machine is usually wide enough to permit two or more sheets to pass through side by side simultaneously. The sheet is guided through the tin bath by the curved guides shown, and by means of the rolls is passed upward through the oil layer. The oil keeps the tin coating on the sheet molten long enough to aid in obtaining a layer as uniform in thickness as possible. It also aids in giving luster by preventing any superficial surface oxidation.

The machine process as just described is not employed for the production of heavily coated tin-plate ("charcoal plate") except perhaps for rather light-gauge sheets. For charcoal plate, a "combination pot" is often used. In this process the sheet is first dipped mechanically in a manner analogous to that described above, after which it is dipped by hand in a pot of pure tin maintained at a rather low temperature, then passed between rolls in the palm-oil bath, whereby the relatively heavy coating of tin is uniformly distributed over the surface.

The tin-coated sheets always carry with them a film of oil as they leave the oil bath. The greater part of this must be removed by a hot alkaline wash and by rubbing with some substance such as bran or middlings. The sheets are then clean and have a high luster. All grades of commercial tin-plate retain some oil on the surface. This serves a useful purpose, however, in retarding the initial corrosion of the sheet, especially during storage and shipment. Such a residual film of oil is not sufficient to be harmful to such operations as lacquering and printing.

Aside from copper wire very little wire is tinned. The process is carried out in a manner quite similar to the zinc-coating of wire.

The tin used in the manufacture of tin-plate is of high grade and no attempt is made to use any additions of metallic ingredients as is not infrequently done in the zinc coating industry. The addition of aluminum, for example, would be expected to be detrimental since sheet tin containing small proportions of aluminum becomes brittle on the surface[11] and may even become so brittle as a result of corrosive attack[12] that it can be broken up into tiny fragments by the fingers. Small percentages of iron, lead, arsenic or antimony are said to decrease the luster of tin and to impart to it a yellowish color.[13] The presence of several per cent of zinc in a tin coating is reported to improve its corrosion resistance, and the addition of iron to the extent of 0.5 to 1.5 per cent increases hardness and wear resistance.[14] The transformation of ordinary tin into its powdery grey allotropic form, which is accelerated at low temperatures, is a rare occurrence although it is said to have been observed on the surface of tinned iron.[15] It may be prevented by the addition of 0.5 per cent of bismuth. Bismuth in proportions up to 10 per cent increases the whiteness and brightness of tin coatings. All such additions, however, if used at all, are for very special products and not for commercial tin-plate.

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[9] Poppleton, C. F., *Iron Age,* **101,** 30, 127 (1918); Camp, J. M., and Francis, C. B., "The Making, Shaping and Treating of Steel," 4th ed., p. 983, Carnegie Steel Company, Pittsburgh, Pa., 1925.

[10] Davis, S. A., U. S. Patent 1,528,407.

[11] Hanson, D., and Sandford, E. J., *J. Inst. Metals,* **56,** 191 (1935).

[12] Heyn, E., and Wetzel, E., *Mitt. Kaiser Wilhelm Inst., Metallforschung,* **1,** 4 (1922).

Ordinarily the "spangle" effect which is so pronounced in zinc coatings is entirely lacking in tin coatings. The crystalline pattern of tin coating can be readily developed by dipping the coated article in dilute hydrochloric acid and this is sometimes done for ornamental effects. Such an etch-pattern is often very pronounced on the inner surface of tin cans in which certain food products have been preserved.

Operating Conditions of Molten Tin Bath

Temperature control of the tin bath is of considerable importance. The usual working temperature of the tin bath is from 600 to 625° F. (315 to 330° C.) while that of the palm-oil layer is 455 to 480° F. (235-249°C.).[16] When the bath consists of two compartments the temperature of the tin in the first one is maintained considerably higher than in the second. For example, a suitable temperature for the tin in the first compartment is 600° F. (315° C.) and in the second 550° F. (288° C.). The need for the somewhat lower temperature in the second compartment arises from the fact that here the palm oil comes in direct contact with the molten tin. If the temperature is too high the oil polymerizes and no longer serves to keep the tin clean. Studies of possible substitutes for palm oil have shown that hydrogenated cotton-seed oil, which does not polymerize, is satisfactory in performance.[17] The consumption of this oil was distinctly less than that of palm oil in a commercial test, although the hardened oil is more expensive. It is understood that hardened whale oil has been found in Germany to be a satisfactory substitute.

The speed at which the sheet is passed through the molten tin in commercial practice is an important factor in determining the amount of tin used in coating a unit area of sheet, or the "tin yield" as it is known in the mill. Formerly a speed of 100 to 120 inches per minute through the tin pot was considered the maximum to be used in tinning coke plate.[10] At present hot-tinning of steel is frequently conducted at speeds up to 300 inches per minute.[7] Increase in speed of the rolls tends to increase the thickness of coating up to peripheral speeds of 250 inches per minute. Increasing the pressure of the rolls decreases the weight of the tin coating, as would be expected.[18]

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[13] Mantell, C., *Mining & Met.*, **10**, 90 (1929).

[14] Maass, E., *Korr, u. Metallschutz.*, **1**, 124 (1925).

[15] Hasslinger, R. v., *Sitzb. Akad. Wein.*, **117**, 501 (1908).

[16] Collins, W. D., and Clarke, W. F., *J. Ind. Eng. Chem.*, **12**, 149 (1920); Williams, I., Paper presented Jan. 23, 1932, Metallurgical Soc., Swansea Tech. College.

[17] Collins, W. D., and Clarke, W. F., *J. Ind. Eng. Chem.*, **12**, 149 (1920).

The thickness of a tin coating is also dependent upon the character of the surface of the sheet, particularly its condition with respect to the degree of pickling received. A sheet roughened by over "pickling" takes on considerably more tin than does a properly pickled sheet, and it is also more difficult to impart a satisfactory luster to such sheets. The adjustment of the exit rolls, that is, their grip on the sheet, is an important factor in determining the uniformity of the coating. As would be expected the hardness or surface condition of the rolls has a definite bearing on the weight of coating; re-tinning or "mending," on the other hand, is without influence.[18]

Structure of Hot-Dipped Tin Coatings

Hot-tinning of iron or copper depends upon the fact that the surfaces of these metals may be wetted by molten tin, just as iron is wetted by molten zinc in the analogous operation of zinc-dipping. In general, it may be said that metals wet other metals with which they form compounds or solid solutions.[19] Tin forms intermetallic compounds with both iron and copper, but it does not appear to form a solid solution with iron at the tin-rich end of the diagram, which is the region of interest in tin-plate.[20] These compounds, $FeSn_2$ in the case of tinned iron, and Cu_6Sn_5 and Cu_3Sn when copper is the coated metal, crystallize out as the coatings are formed. The formation and growth of these interfacial compounds are governed by diffusion of the reactants through the compound layers. While there is still some uncertainty as to the constitutional diagram of the iron-tin system, there is evidence of two compounds other than $FeSn_2$.[21] These are Fe_2Sn and FeSn.

The thickness of the coating on tin-plate is of the order of 1 to 2.5 pounds per base box,* for ordinary coke plate. This corresponds to a thickness range of from 59 to 148 millionths of an inch. The layer of tin-iron compound in such coatings has been found to be approximately 0.00002 inch in thickness.[21a] Although the percentage of alloyed tin will vary somewhat depending upon the operating conditions of the bath, it may be assumed to comprise from 10 to 25 per cent of normal coatings ranging from 1 to 3 pounds per base box.

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[18] Williams, I., Paper presented Jan. 23, 1932, Metallurgical Soc., Swansea Tech. College.

[19] Daniels, E. J., *Trans. Faraday Soc.*, 31, 1277 (1935).

[20] Hoare, W. E., *Proc. Swansea Tech. College Met. Soc.*, page 1, 1934.

[21] Jones, W. D., and Hoare, W. E., *J. Iron and Steel Inst.*, 129, No. 1, 273 (1934).

* As will be explained on page 140 the commercial term "base box" (or "basis box" in England) is weight of coating on 31,360 square inches of sheet or 62,720 square inches of surface to be coated.

[21a] Hoare, W. E., *J. Iron and Steel Inst.*, 129, 253 (1934).

The compound $FeSn_2$, containing 80.9 per cent tin, consists of rectangular crystals which may form rapidly at the steel-tin interface at temperatures as low as 150° C. (302° F.), and are stable up to 496° C. (925° F.). These crystals may be seen at the steel-tin interface in Figure 31. Under certain circumstances the compound becomes dispersed in the tin layer as shown in Figure 32.[22] It is not intended to suggest that these pictures are typical of the structures of commercial coatings, although there is some resemblance to them. As previously indicated, when the initial film of compound is formed the subsequent rate of compound formation is

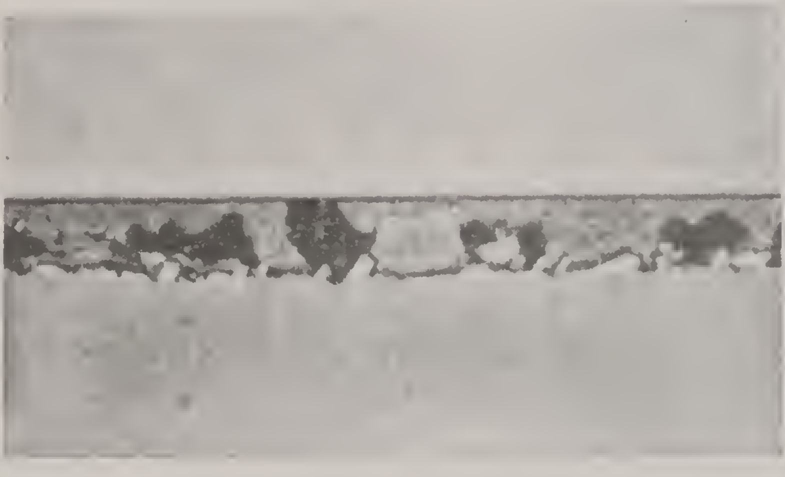

Figure 31.—Hot-Dipped Tin on Steel—Section Showing Alloy Formation. ×500.[22]

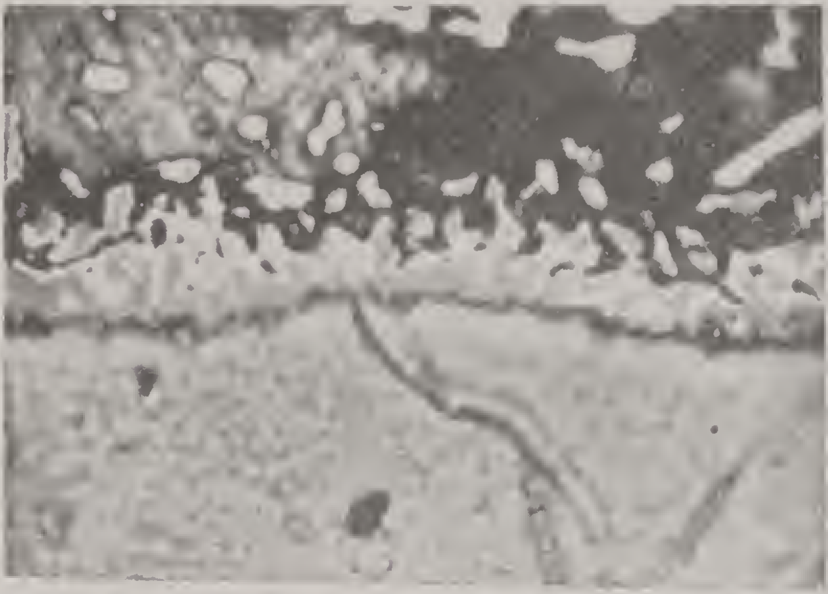

Figure 32.—Hot-Dipped Tin on Copper—Section Showing Alloy Formation. ×1500.[22]

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[22] Daniels, E. J., and Macnaughton, D. J., "Wetting and Detergency," London, Havey, 1937. Reprinted by Internat. Tin Research and Dev. Council, Series B, No. 6.

markedly curtailed. It is for this reason that the compound layer in tin-plate does not attain thicknesses comparable to those of the iron-zinc compounds in zinc-dipped coatings.

The effect of annealing tin-plates above the melting point of tin is to increase the percentage of alloyed tin.[23] This treatment increases the size of the $FeSn_2$ crystallites.[21]

Tin-plate Commercial Terms

The weight of the coating on tin-plate is expressed as the weight of tin per "base box." The base box is essentially a unit of area, and is the equivalent of 112 sheets, 14 inches by 20 inches, that is, 31,360 square inches of sheet or 62,720 square inches of surface to be coated. For coatings of one pound per base box the thickness of tin is 0.000059 in. The term base box originated in the early days of the industry, and was first used with reference to tin-plate of approximately 30-gauge thickness. A base box of material of this gauge weighs approximately a hundredweight, 112 pounds, a fact which is frequently, but erroneously, embodied in the present-day definition of this term. The manufacture of tin-plate is, of course, not confined to sheets of this size, but a great variety of sizes is made. Some multiple of the original "common standard" size, 10 by 14 inches, still is occasionally used for warehouse stocks and some of the higher-grade products. The weight of the tin coating, however, is always expressed in terms of the base box.

The names "coke" and "charcoal" plate are often used in referring to tin-plate. These terms originated in the early days of the industry when the practice was to use sheets made from ordinary puddled iron for the common grades of tin-plate, and sheets of puddled iron made with charcoal for the higher-grade plate. The original significance of the terms has been entirely lost and, as used at present, they refer in a general way to the weight of tin coating. The coke plate is a cheaper product in that it carries a much lighter coating of tin than does the charcoal plate. The weight of coating of tin on coke plate may vary from 1 to 2.5 pounds per base box and on charcoal plate from 3 to 7 and in Great Britain even up to 14 pounds per base box.

Tin-plate is made in a good many different thicknesses; it is necessary, therefore, that the sheet thickness be specified as well as the weight of coating for any particular grade of material. In designating the thickness or weight of the sheet various trade terms, which originated in the early days of the tin-plate industry, are still used, although many of them have lost most of their original significance.

To meet the varied demands of the present day, tin-plate is made to special order in a good many sizes and gauges. The gauge is usually designated by the weight per base box. The lightest-gauge tin-plate is commonly known as "taggers tin." Much of the coke plate which is used largely in the manufacture of tin cans for the canning industry is made in the larger sizes. There is decided need for simplification in the present system used for commercial designation of tin-plate.

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[23] Kohman, E. F., and Sanborn, N. H., *Ind. Eng. Chem.*, **19**, 514 (1927).

Tin-plate is used to a very limited extent for roofing. This should not be confused with terne-plate, a widely used roofing material, which is commonly known as "roofing tin."

Electroplated Tin Coatings

One of the most important recent developments in the field of tin coatings is tinning steel strip by electrodeposition. While the process has been largely on a pilot-plant scale until recently, the product is now understood to be available on a commercial basis.[23a] One factor which has retarded the development is the reluctance of the consumers of tin-plate to accept the electroplated product unless its naturally duller appearance is removed by polishing. As a result, a finishing treatment involving scratch-brushing or buffing has been necessary to produce the customary bright surface.

As indicated on a previous page, development of methods for continuous rolling of steel strip bears directly upon the possibilities of utilizing electro-tinning as an alternative to hot-tinning. In recent years considerable work has been done also on tin plating baths, with the result that information is available on the technical and economic possibilities of electrodeposited coatings. The relatively thin coating of tin provided by the hot-dipping process is readily obtainable by electroplating methods.

Electroplated tin coatings have been used for buckles, brackets, lamp fittings and other small ornamental articles, as well as for larger pieces like fenders and fire screens for producing an appearance resembling oxidized silver. The electroplating process is used also to a considerable extent to renew the coating on tin-coated articles which are used repeatedly in bakeries, confectionery factories and the like.

Tin Plating Baths

Interest in electrolytic tin refining led some years ago to the development of plating baths from which satisfactory heavy deposits could be obtained. Many types of solution including stannous fluosilicate, acid stannous sulfate, stannous chloride, sodium stannite, and sodium stannate were investigated. Of these types of bath only two, acidified stannous sulfate and alkaline stannate, have proved attractive for the production of tin coatings. The possibilities of wider application of electrodeposited tin coatings have led to considerable study of these solutions.

An alkaline tin bath consisting of stannous chloride in a concentrated aqueous solution of sodium pyrophosphate was used as early as 1850.[7] Later, solutions of stannous chloride in potassium hydroxide were devised and baths of this type, containing an addition agent such as glucose, were employed extensively during the World War. Later it was found that more satisfactory deposits could be obtained from an alkaline stannate bath.

[23a] Thomas, C. G. (Thomas Steel Co., Warren, O.), *Private Communication,* Oct. 27, 1938.

Earlier attempts to use stannate baths resulted in the production of spongy deposits due to the presence of stannite ions which decompose, with the precipitation of metallic tin. Successful operation of stannate baths has been obtained by maintaining tin in the quadrivalent state by means of oxidizing agents. This was accomplished first by periodic additions of hydrogen peroxide or sodium perborate.[24] More recently it has been shown that it is possible by the use of insoluble anodes to maintain tin in the stannate condition without additions of oxidizing agents to the bath.[25] Nickel anodes are used for this purpose at intervals following periodic replenishments of tin furnished by anodic solution. A satisfactory alkaline stannate bath may be obtained by the use of 15 to 20 grams per liter of sodium hydroxide and 85 grams per liter of tin in the form of sodium stannate. This bath is operated at 70-75° C. (158-167° F.) and at current densities from 15 to 20 amperes per square foot. It is possible to use current densities up to about 60 amperes per square foot but with some sacrifice of cathode efficiency.

The development of acid tin plating baths, which is comparatively recent, arose from the demand for electro-refined tin. In these baths, the metal is entirely in the bivalent state. One of the first solutions used in electrorefining consisted of stannous fluosilicate containing hydrofluosilicic acid, and glue as an addition agent. Somewhat later the fluosilicate was replaced by sulfate and hydrofluosilicic acid by cresol-sulfonic acid and this solution, somewhat modified, came to be used in tin plating. The tendency of simple acid sulfate baths to yield feathery deposits and to precipitate basic tin compounds is prevented by the use of suitable addition agents. Recent work has shown that a solution of the following composition may be used to obtain very satisfactory tin coatings:[26] 30 grams of tin (introduced anodically), 50-100 grams of free sulfuric acid, 100 grams of cresol-sulfonic acid, 2 grams of gelatin, and one gram of beta-naphthol per liter of solution. This bath is used at room temperature with a current density of 15-20 amperes per square foot; higher current densities (up to 80 amperes per square foot) may be used if the solution is agitated. The solution has good covering power and excellent throwing power, and it operates at nearly 100 per cent cathode efficiency even at the higher current densities.

Electroplating of Steel Strip

As previously stated, considerable interest has developed in the production of tin-plate by electrodepositing tin on steel strip. Both laboratory and plant studies are being made of the feasibility of the process. Plating baths of both the acid type[27] and the alkaline stannate type are under investigation for this purpose. The use of undercoatings of copper and of hot-dipped tin have been suggested as a means of improving the continuity of the tin coating.

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[24] Oplinger, F. F., *Met. Ind. (N. Y.)*, 29, 529 (1931); Wernlund and Oplinger, U. S. Patent 1,919,000 (1933).

[25] Hothersall, A. W., Clarke, S. G., and Macnaughton, D. J., *J. Electrodepositors' Tech. Soc.*, 9, 101 (1934).

[26] Hothersall, A. W., and Bradshaw, W. N., *J. Electrodepositors' Tech. Soc.*, 12, 113 (1937).

[27] Schlötter, M., *Metallwirtschaft*, 14, 247 (1935); British Patent 443,429 (1936); Pine, P. R., U. S. Patent 1,987,749 (1935).

The alkaline stannate bath has been found in general to be more suitable for the production of coatings of low porosity. Its superior throwing power is of no particular advantage in plating strip stock. While acid baths are less satisfactory from the standpoint of continuity of coating, they have the advantage of higher cathode efficiency and metal yield and low bath voltage; moreover, acid baths are operated at ordinary temperatures. It seems probable that it will be possible to electroplate steel strip in the acid bath at speeds comparable to those of the hot-tinning process.[7]

Tin Coatings by the Immersion Process

Tin may be deposited from solution in the form of a very adherent, although very thin, coating without the application of an external electromotive force such as is necessary in ordinary electroplating. The fundamental principle is, of course, the same in both. In this case, however, the necessary current arises from the contact of the dissimilar metals immersed in the solution. The process has found application for small articles of brass, iron or steel such as safety pins, thimbles, buckles, and many other objects for which a bright finish is desired.[28]

In one process the brass articles, after being cleaned, are piled on wire trays, with thin perforated sheets of tin "sandwiched" in at intervals, and are immersed for 3 or 4 hours in a hot (90° C., 194° F.) solution of sodium chloride and potassium acid tartrate (cream of tartar, $KHC_4H_4O_6$). The tin which forms the anode of the couple, passes slowly into solution and is deposited upon the brass articles (cathode). Immersion in a solution of stannous chloride and sodium hydroxide at the same temperature has also been found to be a satisfactory method for coating brass.

In a slightly different process, scraps of zinc are mixed in with the brass articles which are immersed in a solution of stannous chloride and cream of tartar. The zinc is the anode in this case, and as it passes into solution tin is deposited from the solution upon the brass (cathode). The electrolyte, of course, is gradually depleted of its tin. This process is usually carried out in a rotating barrel, and a period of 2 to 4 hours at 80° C. (175° F.) is required.

For tinning iron or steel a slight modification of the method has been found necessary. The solution contains ammonium alum in addition to the substances named above. The solution is kept hot and a period of about 45 minutes is usually sufficient. In all cases the articles are thoroughly cleaned by rinsing with hot water after the plating solution has been drawn off, after which they are dried and polished somewhat by sawdust, bran, or macerated leather. Although the coatings as deposited are very much brighter than those made by electroplating, coatings made by this method are extremely thin but very uniform. It is not possible to form a heavy coating by this method since the deposition of tin necessarily ceases as soon as the surface is covered. Although the method is an old one and is of some commercial importance, it is still carried on in a strictly empirical manner.

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[28] Proctor, C. H., *Met. Ind. (N. Y.)* 12, 64 (1914).

Tinning of Copper

Copper is tinned on a commercial basis both by hot-dipping and by electroplating. A good deal of copper roofing is tinned, usually on one side only, and is generally done by hand. In tinning copper sheet by hand, the cleaned sheet is heated from beneath by some suitable means, and a small amount of flux (ammonium chloride or a solution of zinc chloride) and a few strips of pure tin are dropped on the heated surface. By rubbing with a wad of cotton waste a relatively uniform coating is obtained.[29]

The hot-tinning of copper articles is carried out in much the same manner as the hand-dipping of steel parts. The flux employed is generally an aqueous solution of zinc and ammonium chlorides. The period of immersion in the tin bath is only long enough to bring the article to the temperature of the tin bath and permit free draining of the tin upon removal. The coating so produced invariably contains a small percentage of alloyed copper.[30] At the copper-tin interface a duplex layer consisting of the compounds Cu_3Sn and Cu_6Sn_5 is formed, but this layer breaks up under solvent attack, leading to contamination with copper of both the tin bath and the tin coating. There is evidence that in tinning ordinary copper containing cuprous oxide inclusions a small proportion of copper in the tin bath (about 1 per cent) is conducive to smooth coatings.[30] Cuprous oxide inclusions do, however, contribute to porosity of the tin coatings.[31] Such inclusions are readily removed from the copper surface by cathodic treatment in dilute caustic soda solution.

The tinned copper pipe used in refrigeration equipment is usually produced by hot-dipping.[32] Of late, however, electroplating has come to play a large part in the production of tin-coated copper and brass coils and other parts for refrigerators. Some of this is plated by semi-automatic methods.[33] Both acid sulfate and alkaline stannate baths are used in this work, although the latter seems to be preferred because of its greater throwing power—an advantage in plating parts of irregular shape.

The tinning of copper wire which is to be covered with rubber insulation is a very common practice. The tin layer guards against the corrosive attack on copper by the sulfur in the rubber, and likewise deterioration of the rubber by contact with the copper is prevented to a large extent. Where long life and a continued high degree of adhesion of the rubber are required, tin coatings are, however, inadequate. Pinholes in the tin coating permit the gradual ingress of sulfur vapor and a corrosive attack on the copper follows; this results in loosening of the insulation and acceleration of its aging.

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[29] Krom, L. J., *Met. Ind. (N. Y.)*, 11, 122 (1913); Monroe, H. F., *Metal Worker*, 474, 83 (1915).

[30] Daniels, E. J., *J. Inst. Metals*, 58, 199 (1936).

[31] Jones, W. D., *J. Inst. Metals*, 58, 193 (1936).

[32] Daniels, E. J., and Macnaughton, D. J., *Proc. British Assn. of Refrigeration*, 33, [1] 78 (1936-37).

[33] Shields, A. L., *Monthly Rev., (Am. Electroplaters' Soc.)*, 22, No. 7, p. 15 (1935).

THE USE OF TIN-PLATE IN THE CANNING INDUSTRY

The United States is the largest producer of canned goods in the world. In 1935 these included 164 million cases of canned vegetables and soups, 40 million cases of canned fruits, and 12 million cases of canned fish. Besides these products something like 2 billion pounds of milk and 150 million pounds of meat are canned annually; and even dog food was represented to the extent of 476 thousand cases! In the second year that cans were used for beer about 600 million cans were required. All told, it is estimated that 17 billion containers were made from tin-plate in 1937.

The process of preserving foodstuffs by means of heat was discovered in the late 18th century by Nicholas Appert, who was awarded a prize offered by the French government for a successful method of preserving food for the army.[34] The first mention of the tin-plate container was in a patent granted in England in 1810 to Peter Durand. A few years later William Underwood introduced the canning of fruits and vegetables into New England, but it was not until the time of the Civil War that the industry became well established in America.

The development of the tin can from the crude cannister of Durand down to the latest improvement, the beer can which is capable of withstanding internal pressures, is the work of numerous inventors. When cans were made by hand, the output of an industrious workman under favorable conditions was a hundred a day. At the present time a hundred cans are made with a sequence of machines in a can-making line in twenty seconds.

The tin-plate from which most cans are made is of the coke quality, that is, the thickness of the tin is from 0.00006 to 0.00015 inch. This corresponds approximately to 1 to 2.5 pounds of tin per base box or from 1.0 to 2.5 milligrams per square centimeter of surface.

The fabrication of the simple type of can is accomplished as follows.[35] The bodies (sides) and ends (tops and bottoms) of the cans are cut from sheets of tin-plate, the side seam crimped and then fluxed and soldered from the outside. The two rims of the cylindrical body are curled outward in order that the ends may be sealed on. The bottom is put on by the can manufacturer and the top by the canner, but both by the same method. The rims of the end parts are curled to fit over the ends of the body and a thin film of rubber compound applied in this curl. The sealing operation consists in making a tight double-crimped seam which is made air-tight without the use of solder.

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[34] Macnaughton, D. J., and Hedges, E. S., *Internat. Tin Res. and Dev. Council*, Bull. No. 1, February, 1935.

[35] "The Story of the Tin Can," National Canners Assn., Washington, D. C.

In cans which are enameled on the inside, the enamel is applied to the tinned sheets before fabrication of the can. Two general classes of enamels are used, one to prevent blackening of the cans by the sulfur compounds present in meats and certain vegetables, and the other to prevent the bleaching of certain highly colored fruits. Beer cans are given two coats of enamel and baked twice.[36]

Canned food products range in acidity from about pH 2.6 to pH 6.8. Certain vegetables, notably the legumes and marine products[37] contain sulfur-bearing substances which may react with tin, producing a dark sulfide tarnish, as stated above, and this in turn discolors the contents of the can. Canned cream after some months' storage sometimes induces a "purpling" of the can, which has been shown to be due to a film of tin sulfide.[38]

One of the principal problems of the canned food industry is corrosion of the can. This may take the form either of perforation of the can or of swelling or bulging of the can due to an accumulation of hydrogen liberated by corrosive action. Recent studies indicate that silicon and copper in the steel base in excessive amounts may cause poor resistance to perforation in fruit packs.

Corrosion Resistance of Tin Coatings

Performance in the Atmosphere

Upon exposure to the air tin becomes coated within a few hours with an invisible film of stannic oxide which greatly retards but does not prevent continuation of attack. Weight increment studies of specimens exposed indoors show that after the first three or four days the gain in weight with time is a linear function. This suggests that after the initial period the surface film is of a granular nature and not of the continuous protective type. It will be recalled that an analogous behavior is shown by zinc, although the actual value of the weight increment after 220 days in a comparative test indoors at Birmingham (England) was but 0.8 milligram for tin as against 3.0 milligrams for zinc for surface areas of 1 square decimeter.[39] When the tin surface was freshly scraped before the test there was a gain in weight of 1.2 milligrams. Undoubtedly the prevailing character of the atmosphere has an influence on specimens exposed indoors. For instance, at the end of 215 days, specimens of tin sheet exposed in telephone central offices at the following locations had gained in weight in milligrams per square decimeter of area as follows: Asbury Park, N. J., (sea-

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[36] "The Development of a New Container—The Beer Can," an address by W. E. Taylor, The American Can Company, before Food Technology Conference, Mass. Inst. Tech., Sept. 15, 1937.

[37] Dill, D. B., and Clark, P. B., *Ind. Eng. Chem.*, **18**, 560 (1926).

[38] Jackson, C. J., Howat, G. R., Hoar, T. P., *J. Dairy Research*, **7**, 284 (1936).

[39] Kenworthy, L., *Trans. Faraday Soc.*, **31**, 1331 (1935).

Table 14.—Atmospheric Corrosion of Tin.

Location	Original Weight	Change in Weight, Grams			Tensile Properties after 6 Yrs.		% Change in Tensile Properties		Remarks
		1 Yr.	3 Yrs.	6 Yrs	Tensile Strength	Elongation (%)	Tensile Strength	Elongation (%)	
Pittsburgh	464.38	+0.33	+0.39	.....					Severely distorted; deposit of some tar and silt. White spotty film, gray near edges. (One specimen missing.)
No. 1	463.64	+0.32	+0.66	+1.45	3035	61.8	−12.0(*4.3*)*	−1.0(*17.6*)	
Altoona	469.01	+0.45	+1.27	+2.42	2940	61.5	−14.8(*3.2*)	−1.4(*19.7*)	Black heavy film with white pitted scale, tinge of red (foreign source) at edge.
No. 2	462.55	+0.46	+1.27	+2.57					
New York City	470.83	+0.50	+0.89	+1.48	3061	60.7	−11.3(*3.0*)	−2.7(*24.6*)	Dirty dark gray film, small amount white pitted scale.
No. 4	470.43	+0.52	+0.92	+1.49					
Rochester	464.92	+0.33	+0.53	+0.87	3145	59.1	−8.9(*2.2*)	−5.3(*14.7*)	Spotty whitish tarnish, few pits.
No. 6	466.23	+0.32	+0.55	+0.88					
Sandy Hook	470.64	+1.04	+1.24	+2.20	2945	41.1	−14.6(*3.4*)	−34.1(*15.2*)	Surface speckled with white scaly spots with pits beneath.
No. 5	472.62	+1.00	+1.19	+2.07					
Key West	465.64	+0.43	+1.12	+2.74	3002	57.3	−13.0(*2.3*)	−8.2(*17.5*)	White speckled film with scale at edges.
No. 7	467.58	+0.47	+1.17	+2.82					
La Jolla	470.68	+1.50	+2.40	+3.87	2788	20.8	−19.2(*4.1*)	−66.8(*26.3*)	Spotty white scale areas with pitting, yellowish spots in heaviest scale.
No. 9	468.04	+1.45	+2.16	+3.71					
State College	469.23	+0.19	+0.22	+0.25	3157	68.5	−8.5(*2.8*)	+10.1(*16.2*)	Light film with white pitted scale.
No. 3	471.13	+0.17	+0.21	+0.23					
Phoenix	467.84	+0.14	+0.19	+0.34	2997	59.2	−13.1(*1.8*)	−5.1(*21.2*)	White speckled film, slight pitting.
No. 8	470.34	+0.14	+0.20	+0.93					

* Italic figures in parentheses indicate maximum percentage difference due to chance.

side) 0.151; New York City (industrial) 0.114; and Rockaway, N. J. (rural) 0.089. These specimens had been carefully cleaned for the test by abrading under water with levigated alumina, washing in water and then alcohol and quickly drying.

The behavior of tin exposed directly to the outdoor air is influenced by rainfall, atmospheric pollution and particularly by chlorides which are prevalent in marine locations. In Table 14 are given the values after 1, 3 and 6 years for change in weight and change in tensile strength and percentage elongation of tin specimens exposed to the atmosphere in nine localities by Committee B-3 of the American Society for Testing Materials.[40] The area of the specimens employed in the gravimetric tests was 216 square inches, (13.9 dm^2). It will be recalled that Pittsburgh, Altoona and New York City are industrial in character, Rochester urban, Sandy Hook, Key West and La Jolla, marine, and State College and Phoenix rural, the latter being in an arid region. It should be mentioned that the test specimens at Pittsburgh were submerged under 10 feet of flood-water for several days during March, 1936, which date is between the third and sixth year period of exposure.

It will be observed that the three marine locations provided the most corrosive conditions; this is shown particularly by the loss in percentage elongation. Industrial atmospheres appear to be definitely more severe in attack on tin than do the less polluted country atmospheres. The outdoor air of Birmingham is even more corrosive than that of any of the American industrial localities given in Table 14, the weight increment obtained after one year of exposure being 66 milligrams per square decimeter, or 0.92 gram calculated to the areas employed in the A. S. T. M. test. The relative humidity of the atmosphere apparently has little accelerating effect upon the corrosion of tin until it attains a value of 85 per cent. This conclusion is based upon the results of an experiment on the deliquescence of corrosion products detached from a corroded specimen of tin.[39]

The corrosion of tin-plate exposed to the atmosphere is characterized mainly by rusting at pinholes in the coating. As is well known, iron is anodic to tin under conditions of exposure to the atmosphere and when immersed in water and many solutions. Unlike zinc, tin does not protect iron cathodically in these environments. Consequently the performance of tin-plate is determined largely by its porosity. All commercial tin-plate whether of the coke or charcoal variety is porous or discontinuous. Although it is claimed that coatings of the order of 100 grams per square meter (approximately 9 pounds per base box or 0.0005 inch in thickness) can be produced free from pinholes,[41] this is difficult to accomplish on a commercial scale. In an investigation of the relation of coating thickness to porosity, it has been reported that the number of pores per 100 square centimeters falls from 8000 to 300 as the thickness of coating is increased from 1 to 3 pounds per base box. Further improvement is obtained with greater difficulty since increasing the coating thickness to 15 pounds per base box reduced the number of pores from 300 to 2.[42]

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[40] Finkeldey, W. H., *Proc. Am. Soc. Testing Materials*, 38, (1938).

[41] Peter, F., and Le Gal., G., *Archiv. Eisenhüttenwesen*, 9, 285 (1935).

Pores in tin-plate arise from a variety of causes. Among the factors which may be responsible are surface cleanness of steel sheet, pickling procedure and cleanness of the flux. It has been suggested that the occurrence of pinholes may be due to hydrogen absorbed in the pickling operation which is then liberated upon tinning.[43] Other investigators have disputed

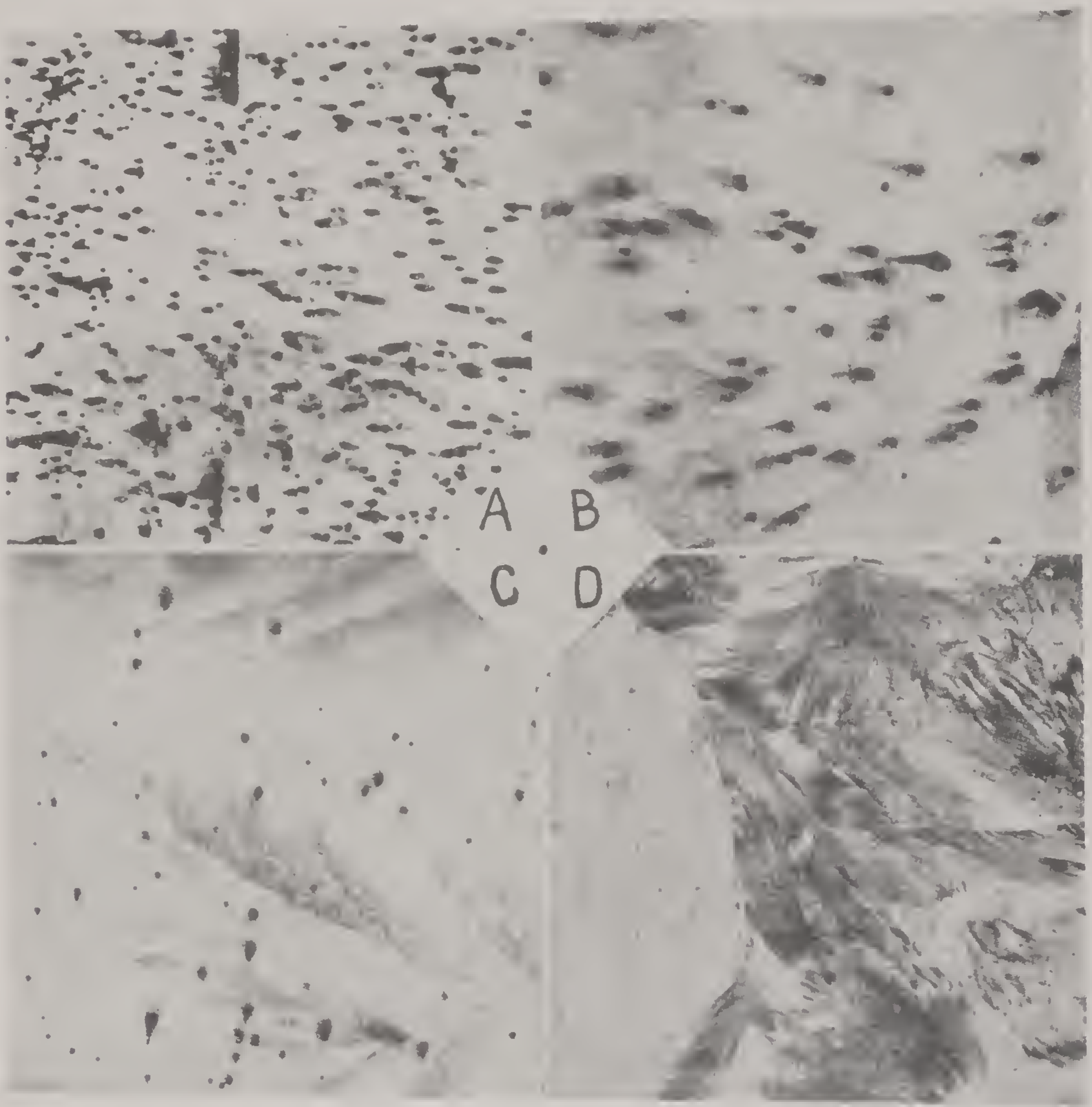

Figure 33.—Porosity of Composite Coatings of Hot-Dipped and Electrodeposited Tin (After Hot-Water Test).[45]

A. Blank Tin-Plate 1.5 lbs. per Base Box. 1150 Pores per sq. dm.
B. As (A) with 0.25 lb. Electrodeposited Tin per Base Box. 116 Pores per sq. dm.
C. As (A) with 1 lb. Electrodeposited Tin per Base Box. 76 Pores per sq. dm.
D. As (A) with 8 lb. Electrodeposited Tin per Base Box. No Pores.

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[42] Hoare, W. E., *J. Iron and Steel Inst.*, 136, 99 (1937).

[43] *Mitt. Materialprüfungsgamt und Kaiser Wilhelm Inst. Metallforschung*, new series No. 3, p. 58 (1926).

this explanation of the origin of pinholes[41] but it is generally conceded that evolution of hydrogen is a factor in blistered coatings. The occurrence of pinholes in electrodeposited coatings may be caused either by the character or cleanness of the steel surface, or by factors associated with the plating bath and its operation, such as, for example, suspended dirt particles, precipitation of basic salts, etc.

The porosity of tin-plate may be reduced by superimposing an electrodeposited layer of tin upon the hot-dipped product.[44] This has been done from an alkaline bath with the following results:[45]

Tin added by plating (lb./base box)	nil	0.25	1.0	2.0	4.0	8.0
Porosity (pores/sq. dm.)	1000	135	44	30	5	0

The behavior of the composite coatings on outdoor atmospheric exposure was in line with the porosity results. Their average porosity was found to be from 5 to 10 per cent of that of hot-dipped coatings of the same thickness. A comparison of the pores in these coatings revealed by testing them in hot water is shown in Figure 33.

The deformation of tin-coatings incident to the fabrication of articles from tin-plate may have a serious effect upon their protective value. A microscopic study indicates that forming and drawing operations cause surface fractures in the steel base which in turn cause discontinuities in the tin coating. A comparative study[46] made recently on hot-dipped and plated coatings has shown that the resistance to increase in porosity by deformation produced by stretching was strikingly different from the order of protective value of the various coatings in the unstretched condition. The average values of porosity obtained for the various unstretched tin coatings in this study are given in Table 15. The rough matte deposits from the acid bath were obtained from baths containing an inadequate percentage of addition agents, the smooth matte when the bath contained an intermediate amount of such agents, and the bright (actually semi-bright) from solutions containing a relatively high proportion of addition agents.

Table 15.—Porosity of Tin Coatings of Various Types of Tin Coatings.

	Pores for sq. dm. for coatings of thickness	
Type of Coating	0.00012 inch	0.0003 inch
Hot-dipped (tin-plate)	616	156
"Alkaline" tin deposit	646	32
Composite (1:3 electrodeposited tin: hot-dipped tin)	98	5
Rough matte "acid" tin deposit	1034	200
Smooth matte "acid" tin deposit	530	42
Bright "acid" tin deposit	393	40

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[44] Macnaughton, D. J., British Patent 417,411 (1933).
[45] Hothersall, A. W., and Bradshaw, W. N., *J. Soc. Chem. Ind.*, 54, 320T (1935).
[46] Macnaughton, D. J., and Prytherch, J. C., *J. Electrodepositors' Tech. Soc.*, **12**, 66 (1937).

The superiority of the composite coating is again demonstrated in these results. It is evident also, as has been pointed out previously, that deposits from the alkaline plating bath are usually somewhat less porous than are those from acid solutions.

The porosity results obtained upon stretching the lighter-weight coatings listed in Table 15 are shown in Figure 34, in which the number of

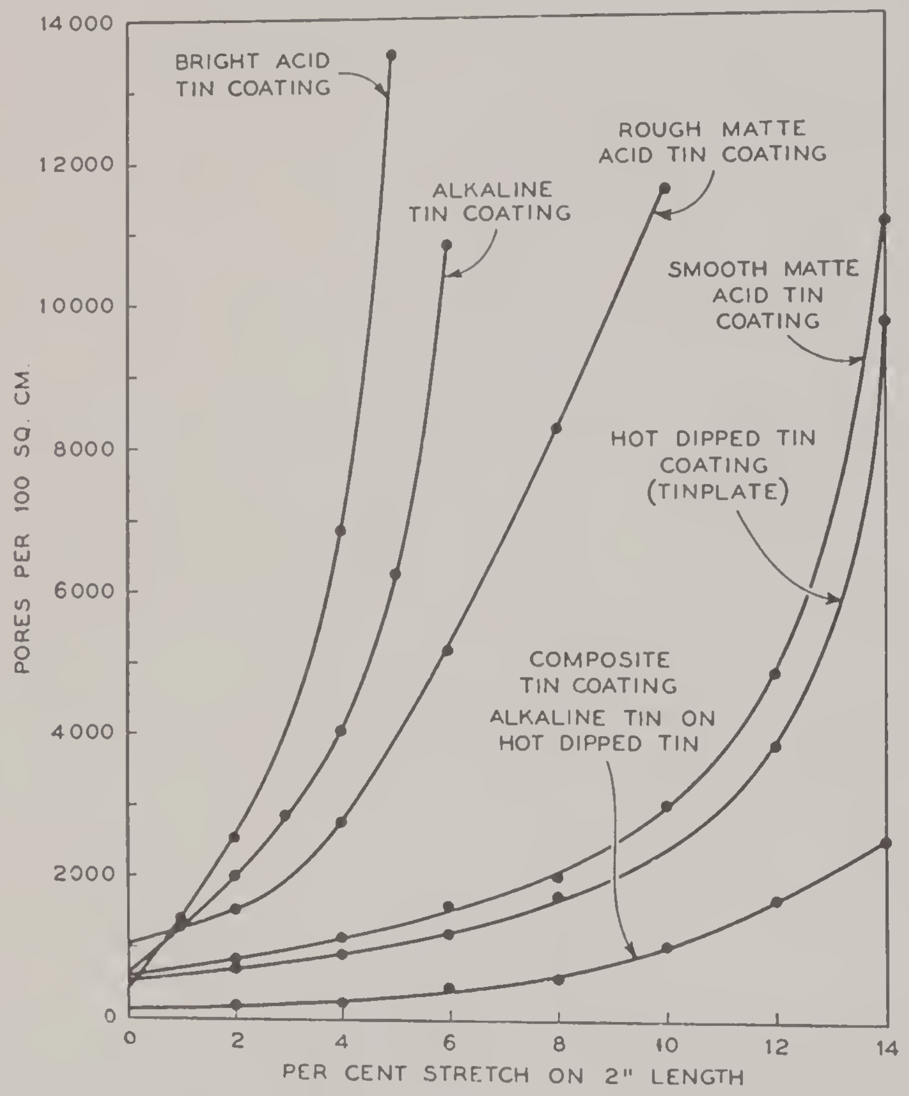

Figure 34.—The Effect on Porosity of Stretching Tin Coatings Approximately 0.00012 Inch Thick on Mild Steel, Approximately 0.1 Inch Thick.[46]

pores developed in the hot water test (described in Chapter 12) are plotted against per cent stretch on specimens 2 inches in length and 0.5 inch in width. The values for the heavier coatings (0.0003 inch) subjected to the same treatment were found to fall in the same order as the values for the lighter coatings here shown, although of course the range of porosity was much lower.

The performance of the composite coating is shown to be outstandingly good. From the standpoint of cost, however, it seems unlikely that such coatings can be used for such articles as tin cans. It is of interest to note that the smooth matte coating from the acid bath behaves most nearly like that produced by hot dipping.

The severe local porosity caused by bending tin-plate may be reduced by the subsequent electrodeposition of tin on the bent surface.[45] For example, it has been reported that the porosity of bent tin-plate of 1.25 lb. per base box quality on which 0.25 lb. (2.8 g. per sq. m.) of tin has been electrodeposited subsequent to bending is similar to that of a hot-dipped coating of 10.5 lb. per base box quality. It has long been common practice in the manufacture of the better grade of articles from tin-plate, such as kitchen utensils, to retin them after fabrication, but this has usually been done by means of hot-dipping; presumably this might well be accomplished by electroplating.

A distinction is usually made between normal pores, which are cavities extending through the tin coating to the steel base, and what is known as potential pores, which are defects in only the outer tin layer of the coating. Careful optical studies made on a specimen of tin-plate with a coating thickness of 0.00018 inch showed that in a particular instance the diameter of the affected area of the coating in the case of normal pores was 0.0125 inch, while the diameter of the steel base exposed was 0.002 inch.[47]

Potential pores at low magnifications appear to be areas of increased roughness. The term includes grease lines, which are regions in which much of the tin has been stripped by runnels of oil formed in the nip of the top pair of grease-pot rolls; it also includes mottle or "dry patches" which are areas of exposed $FeSn_2$ crystallites produced in some obscure manner.[48]

The degree of protection against corrosion afforded by potential pores is considerable unless the coating is subjected to mechanical operations such as drawing, forming, bending, etc. Under these circumstances the $FeSn_2$ layer, owing to its brittle nature, breaks down and exposes the underlying steel base.

If the mottled area is extensive it may cause a sheet of tin-plate on which it appears to be rejected as a "mender." In the inspection of the finished plates, which is a "100-per cent" inspection, the sheets are classed as (a) primes, (b) seconds, (c) menders, and (d) waste. The "prime" sheet is not a perfect sheet, but in general is as good as can be made by present means for the particular grade of plate under consideration. The "menders" are sheets which by being retreated, usually by redipping in the molten tin, after a little cleaning, can be improved and put into class (a) or (b); the "waste" is, as the name implies, more or less of a loss although, in the form of strips and other small pieces, much of it is salable. The "seconds" were formerly known as "wasters," a term often not clearly understood by the purchaser. A "second" is a sheet which because of certain defects, usually of limited extent, requires that extra care be taken in its usage. For can making, for example, if a second has only a ragged edge it is for all practical purposes as good as a prime sheet. If it contains a number of bare spots, the part remaining after discarding the bare areas is essentially the same as the first-class sheet. For some uses, however, which require an entire sheet, second sheets can not be considered at all.

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[47] Hoare, W. E., and Chalmers, B., *J. Iron and Steel Inst.*, 132, No. 2 (1935).

[48] Hoare, W. E., *Proc. of Swansea Tech. College Met. Soc.*, Reprinted by Internat. Tin Res. and Dev. Council, *Series A*, No. 14 (1934).

The surface of hot-tinned sheets sometimes has an undulating or wave-like contour in the direction of tinning. These "ripple" marks have been found to consist of parallel ridges and valleys in the tin coating (at right angles to the direction of tinning). In one specimen, examined by means of an optical method involving the formation of interference fringes between an optical flat and the tin surface, it was found that the half-depth of the valleys was approximately one-third of the mean coating thickness.[47] There is also a somewhat similar effect of ridges and valleys in the coating lying *along* the direction of tinning.

"Yellow stain" is the name given to a golden yellow coloration which occasionally develops on the surfaces of tinned sheets after 3 or 4 months of storage. The stain may appear in patches or over most of the area of the sheet, except the edges which are usually free from it. It is a film strongly adherent to the tinned surface and cannot be removed by heat, organic solvents or dilute acids or alkalies. Apart from the unsightly appearance of yellow stain it renders sheets unsuitable for lithographing purposes since the stained portions are not wettable by ink. As far as is known, yellow stain does not reduce the resistance of tin-plate to corrosion in the atmosphere and most solutions.

A recent investigation [49] has elucidated the mechanism of the formation of yellow stain and suggested a practical method of its removal from sheets. The resemblance of the stain to the oxidation tint on tin suggested that the stained areas were in reality regions of superficial oxide; and it was found experimentally that it was possible to produce by differential aeration in an electrolytic cell a yellow oxide film identical in appearance with the natural stain on commercial tin-plate. The film appeared on the anode of the cell, while the cathode around which oxygen was bubbled remained in its highly polished condition. Furthermore, it was found that both the experimentally formed film and the natural yellow stain could be removed readily by cathodic reduction—a result which indicated the practical usefulness of this method for the treatment of affected commercial sheet. In view of these results it is reasonable to assume that yellow stain is produced by differential oxidation arising from conditions which affect the uniformity of exposure of the surface of the sheet to the air. Factors such as the distribution of oil or grease over the sheet or uneven contact with sheets or objects may well, under conditions of moderately high humidity, induce such differential oxidation.

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[49] Beynon, C. E., Leadbeater, C. J., and Edwards, C. A., *Tech. Pub. Internat, Tin, Res. and Dev. Council, Series D,* No. 1 (1935).

Performance in Aqueous Solutions

It may be inferred that the relationships between defects characteristic of tin coatings (such as porosity) and corrosion resistance, which have been discussed in the previous section dealing with atmospheric exposures, are valid for tin-plate submerged in water and aqueous solutions. It is true that in the majority of solutions the exposed areas of iron rust, a notable exception being in solution of certain organic acids in which, as will be described later, tin corrodes in preference to iron. Inside of tin cans and in the absence of air continuity of coating is less essential than it is in outdoor exposures.

Pinhole corrosion of tin-plate has always been a disadvantage in its use for certain kitchen ware and utensils, with the result that years ago vitreous enamel coatings, glassware and aluminum had little difficulty in invading the field. However, tin-plate still finds wide use because of its cheapness. The use of tin-plate for baking dishes presents no difficulty since the pores become plugged with grease.

The resistance of block tin to water is responsible for its use in pipes and equipment for handling distilled water. Carbonated water, also, has practically no solvent action on tin. This is in considerable contrast to lead which is readily corroded in distilled water. Even in sea-water tin is corroded markedly less than are the other common non-ferrous metals.[50] Tin-plate, on the other hand, usually develops pinhole corrosion, particularly in saline solutions if air is present. It is true that the air-formed film on tin-plate affords a measure of protection for short periods of exposure to water and neutral salt solutions.

In the use of tin-plate in nearly neutral solutions, such as water, dairy products and certain canned foods, corrosion of a localized type characterized by "black spots" occurs. These spots are black by diffuse light but may appear grey by oblique light. They are irregular in shape and usually extend along scratches in the plate. These spots may vary from microscopic sizes to areas of one or two square centimeters. It is easy to produce "black spots" experimentally by immersion of tin-plate in neutral salt solutions. The presence of copper as an impurity promotes development of the spots although it is not essential for their appearance, since similar behavior is exhibited by tin of high purity.

The mechanism of the formation of "black spots" has been studied by electromechanical methods.[51] It was found that before the development of the spot, the tin surface becomes more noble, owing to the repair of any defects in the air-formed film. The repairing process is one of anodic oxidation, since defects in the film become anodic areas upon immersion. When, however, the anodic area at the base of a pit becomes sufficiently polarized due to deficiency of anions, it is suggested that dissolution of stannous ions occurs, causing undermining and breakdown of the film. The point of breakdown then becomes a microscopic anode of sufficiently high anodic current density to produce a black spot of oxide. By chemical analysis the black corrosion product has been shown to consist of a mixture of stannous and stannic oxides, mainly the former.

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[50] Friend, J. N., *J. Inst. Metals*, 39, 111 (1928).

[51] Brennert, S., *Tech. Pub. Internat. Tin Res. and Dev. Council, Series D*, No. 2 (1935); Hoar, T. P., *Trans. Faraday Soc.*, 33, 1152 (1937).

Tin is corroded rapidly in strong alkalies, the attack apparently increasing progressively with increase in alkalinity beyond about pH 8.5 [52] and in ordinary acids exposed to the air; it is rather resistant to attack by dilute acids in the absence of air, as is illustrated in Table 16.[53] The process of corrosion in the latter case is controlled by the rate of cathodic depolarization, and since the hydrogen overvoltage of tin is high, the rate of corrosion is low in the absence of depolarizing agents such as oxygen (or nitrate in the nitric acid solution). In higher concentrations of strong acids tin corrodes more readily owing to the development of corrosion cells of sufficient potential to discharge hydrogen at tin cathodes. The presence in tin of metallic impurities of lower hydrogen discharge potential should increase corrodibility, particularly in acids. The deleterious influence of copper which was observed [54] when copper-bearing tin specimens were immersed in dilute hydrochloric and citric acids exposed to air might be expected to persist in the absence of air.

Table 16.—Corrosion of Tin in Ordinary Acids.

		Mg. per sq. dm. per day	
Acid	Conc. %	Hydrogen	Oxygen
Nitric	3	630	640
Hydrochloric	6	60	11,100
Sulfuric	6	35	4,300
Acetic	6	15	2,300

The behavior of the tin-iron couple, as exemplified in tin-plate, has been the subject of considerable investigation. The matter is of particular importance in connection with the use of tin cans in the fruit canning industry. It would be expected from the acidity of these products, and the electrode potential relationship of tin and iron, that perforation of cans would be very common. While it is true that some of the more acid fruits, notably Bing cherries and certain berries, do give trouble, particularly if stored at relatively high temperatures,[55] perforation of cans is not a source of serious loss. It is clear, from general experience in the canning industry, that anodic dissolution of the exposed steel base at pores in the tin coating is either retarded or entirely prevented.

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[52] Derge, G. J., *Am. Inst. Mining Met. Eng. Tech. Paper*, No. 913 (Feb., 1938).
[53] Whitman, W. G., and Russell, R. P., *Ind. Eng. Chem.*, 17, 348 (1925).
[54] Hoar, T. P., *J. Inst. Met.*, 55, 135 (1934).
[55] Kohman, E. F., *Nat. Canners' Assoc. Bull. 22L*, p. 11 (1927).

Electromotive force measurements of the tin-iron couple some years ago disclosed an unsuspected variability of behavior.[56] First observed in several strong electrolytes and later in certain fruit juices and organic acids, this variability of e. m. f. was recognized as having a bearing upon the problem of tin can corrosion. The measurements showed that the iron in the tin-iron couple was initially anodic, a relationship to be expected, but within a few minutes a reversal of potential occurred in which the iron became cathodic and remained so. A later more exhaustive investigation of the phenomenon[57] employing current-time, potential-time, and loss of weight measurements has been illuminating. A summary of the results obtained for the direction and magnitude of current in the couple is given in Table 17. In every case (although not shown in the table), tin and iron gave initially high (noble) potentials which fell rapidly to low values. Evidently the first effect is the breakdown of the initial oxide film. The results compiled in Table 17 show that, following the film breakdown, iron is initially anodic in the presence of citrates but becomes cathodic in time, while the reverse behavior is shown for the couple in sulfuric acid. In oxalic acid, however, iron is the cathodic element throughout the experiment. Couple current studies in citric acid, made as a part of this investigation, showed that the current rose rapidly to a high value after the reversal of potential and then fell rapidly to a small constant value of a few microamperes which was appreciably less in the absence of air than under conditions of air saturation. The results of corrosion tests on tin and iron alone and coupled together made in dilute solutions of citrate ions at pH 2.0 and at pH 5.0 are given in Table 18. Experiments were conducted both in the presence and in the absence of air.

Table 17.—Direction and Magnitude of Current in Tin-Iron Couple in Dilute Acid Media

In 0.1*M* citric acid:	Iron initially anode, became cathode after 5-10 sec. Current after 5 mins.: c. 0.75 ma.
In 0.1*M* citrate buffer:	Iron initially anode, became cathode after 40-100 secs. Current after 5 mins.: c. 0.25 ma.
In 0.1*M* oxalic acid:	Iron cathode throughout. Current after 5 mins.: c. 1.0 ma.
In 0.01*M* sulfuric acid:	Iron initially cathode, became anode after c. 1 sec. Current after 5 mins.: c. 0.3 ma.

From the foregoing account it becomes possible to understand the behavior of tin-plate in the presence of dilute acids when exposed to the air and when used in sealed containers. The initial polarity of the couple

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[56] Mantell, C. L., and King, W. G., *Trans. Am. Electrochem. Soc.*, 52, 435 (1927); Kohman, E. F., and Sanborn, N. H., *Ind. Eng. Chem.*, 20, 1373 (1928); Lueck, R. H., and Blair, H. T., *Trans. Am. Electrochem. Soc.*, 54, 257 (1928).

[57] Hoar, T. P., *Trans. Faraday Soc.*, 30, 472 (1934).

Table 18.—Corrosion of Tin and Iron Alone and in Couple.

Weight loss in 48 hours. Temperature 18-22° C.
Mean of Duplicates.

1		2	3	4	5	6	7	8	9	10	11	12
	Liquid Corroding	Quantity of Electricity Passed by Couple Coulombs	Sn Alone mg.	Sn with Fe in same Vessel mg.	Sn Coupled to Fe mg.	Increase of Sn Corrosion Caused by Coupling mg.	Weight of Sn^{++} Equivalent to Quantity of Electricity Passed mg.	Fe Alone mg.	Fe with Sn in same Vessel mg.	Fe Coupled to Sn mg.	Decrease of Fe Corrosion Caused by Coupling mg.	Weight of Fe^{++} Equivalent to Quantity of Electricity Passed mg.
Air-Saturated	0.1*M* citric acid pH 2.0	4.03	2.25	2.1	4.2	2.1	2.4	3.95	2.5	1.1	1.35	1.2
	0.1*M* citrate buffer pH 5.0	5.15	0.9	0.9	3.9	3.0	3.1	1.4	3.0	1.55	1.45	1.5
Air-Free	0.1*M* citric acid pH 2.0	2.88	0.2	0.2	1.95	1.75	1.75	4.95	2.9	0.55	2.35	0.85
	0.1*M* citrate buffer pH 5.0	1.19	0.3	0.3	1.0	0.7	0.7	3.7	2.15	0.3	1.85	0.35

depends upon the relative potentials of the two metals coated with air-formed films. In sulfuric acid the oxide-coated iron electrode is the more noble, while in citric acid the reverse is the case. Upon dissolution of the films the potentials of the electrodes fall to values characteristic of the bare metals in the given electrolytes. In the presence of citrates and oxalates (and certain other organic acid radicals) tin forms stable complex ions restricting thereby the concentration of stannous ions and in consequence rendering the tin electrode markedly electronegative and anodic to iron. On the other hand, in sulfuric acid no complexes are formed, and the two metals stand in the general relationship to each other shown by their standard electrode potentials.

It is evident that in the tin can, where relatively oxygen-free conditions prevail, the rate of corrosion will be controlled by the rate of hydrogen evolution at cathodic areas. The foregoing work and that of earlier investigators has shown that in cans containing fruit acids the cathodic element is iron. Owing to the low hydrogen overvoltage of this metal sufficient hydrogen may be discharged to cause what is known as a "springer" or a bulging of the can. Since, however, but a small percentage of the pack develop springers, it is evident that the tin-iron cell is largely in a state of polarization. This fact suggests that substances are present in the food products which inhibit the cathodic discharge of hydrogen on iron in a fashion analogous to that produced by the use of organic inhibitors in the pickling of steel. As a matter of fact, it has been observed [58] that gelatin inhibits corrosion in canned fruits of high acidity but is without effect at low acidities. It will be recalled that the isoelectric point of gelatin is at pH 4.7 and that for acidities greater than that (lower values of pH) it is positively charged and migrates cataphoretically to the cathode. It seems evident, therefore, that this behavior of gelatin as a cathode inhibitor is illustrative of the mechanism by means of which corrosion of cans in highly acid media is retarded.

Perforation of the can at pores in the coating is minimized under the conditions mentioned in the foregoing discussion for the reason that the exposed iron areas are afforded cathodic protection. The addition of citric acid to fruits of low acidity has been shown to reduce corrosion markedly,[59] and this appears to be due to an increase in the efficiency of cathodic protection obtained in this manner. The greater tendency toward perforation reported for lacquered cans [60] may be due to the absence of cathodic protection at pores in the tin coating not covered with lacquer.

There is always a certain amount of corrosion of both tin and iron induced by local cell action on each metal. This accounts for the fact that salts of both tin and iron are found in the food products. Although there has been some controversy as to the toxicity of tin present in canned food, the consensus of opinion is that the quantities likely to be consumed are not harmful.

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[58] Morris, T. N., and Bryan, J. M., *Dept. Science and Ind. Res. Food Invest.*, Spec. Report 40 (1931).

[59] Kohman, E. F., and Sanborn, N. H., *Ind. Eng. Chem.*, **25**, 920 (1933).

[60] Kohman, E. F., *Food Manuf.*, **4**, 292 (1929).

RECOVERY OF TIN FROM TIN-PLATE SCRAP

On account of the high price of tin and the very low price of tin-plate scrap, the recovery of the tin from such scrap has long been a subject of study and investigation. A great number of patents have been granted but only a few of the suggested methods have proved successful in practice on a commercial scale.

The early methods, which were based upon the use of such solvents as ferric chloride and stannic chloride, were too expensive and hence unsuccessful commercially. Likewise the "dry" metallurgical method of partially melting off the tin, together with oxidizing some of it to the form of "tin ashes" from which the tin was later reduced, was not a success. The two commercial methods used with considerable success today are (a) electrolysis in an alkaline solution and (b) treatment with dry chlorine.

In the electrolytic method, the tin-plate scrap, after being cleaned, usually with a hot solution of sodium carbonate, is compressed into bales of suitable size for handling. It is then made the anode of an electrolytic cell of which the other electrode may be a copper grid or the iron container for the solution. The electrolyte is a solution of sodium hydroxide containing some oxidizing reagent and is kept at approximately 70° C.)160° F.).

Tin is dissolved at the anode to form sodium stannite, from which tin is recovered at the cathode in a finely divided condition as a spongy deposit which after removal may be compressed, dried and melted. Experience has shown that a considerable excess of sodium hydroxide as well as of oxidizing reagent over the theoretical amount must be used. The bales of scrap, freed from the tin, are melted and used in the preparation of such products as sash weights. The use for steel making of scrap of this nature which may sometimes contain appreciable amounts of tin is not favored in American steel practice.

The tin may also be recovered from tin-plate scrap by means of an oxidizing alkaline solvent, such as sodium hydroxide and sodium nitrate, without electrolysis. By keeping the solution at the boiling point for several hours sodium stannate crystallizes from the solution, and can be separated from the liquid by a centrifuge. The stannate is usually converted to the form of tin oxide and is used in this form, principally in the enameling industry.

The chlorine treatment depends on the fact that *dry* chlorine at low temperatures readily reacts with tin but not with iron. The anhydrous stannic chloride which is formed drips off the clean baled scrap and is recovered and used as such. No attempt is made to obtain the tin from this, as the tetrachloride finds a ready market, particularly in the silk industry. Although the difficulties attendant upon this process are very great, the process has been developed so that now it is decidedly a commercial success.[61]

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[61] Anon., *Met. Chem. Eng.*, 17, 187 (1917); Mason, M., *Met. Ind. (London)*, 23, 338 (1923).

Chapter 9

Nickel and Chromium Coatings

NICKEL COATINGS

Nickel has been used for many years as a protective and decorative coating for brass, iron and steel. It is applied to fabricated articles or parts, and recently, to sheets and wire. The method of application is largely by electroplating, although nickel-clad sheet produced by hot-rolling layers of nickel and steel in intimate contact is coming into commercial use. Nickel coatings may be obtained by spraying and this method of application, as well as electroplating, is finding increasing use in building-up worn surfaces. Nickel may be applied also by evaporation and sputtering methods, although nickel coatings so formed have not attained commercial importance.

Nickel possesses a combination of physical and chemical properties which make it widely useful as a coating metal. In strength, hardness and ductility it approaches mild steel, and nickel-clad steel is readily welded and hot-worked. Nickel is a relatively noble metal which maintains a more or less permanent white appearance in the air and possesses a high degree of resistance to corrosion by natural waters, sea-water, and neutral and alkaline salt solutions. Since nickel is not appreciably attacked by fruit acids, vegetable brines, dairy and meat products, and since its salts are considered to be non-toxic,[1] nickel and nickel-coated equipment is extensively used in the food industries.[2] The principal limitation of nickel as a coating metal lies in its electropositive relationship toward iron in most environments, a fact which makes necessary the use of relatively pore-free coatings for satisfactory protection of the basis metal.

With the development and widespread use of chromium plating in the past decade, nickel has assumed increased importance in its extensive use as an undercoating for this metal. Chromium coatings alone, in the thickness which is comparatively feasible, do not provide adequate protection to ferrous metals and consequently it is common practice to employ a protective undercoating which is usually nickel or a composite layer consisting of copper and nickel. It is customary to buff this undercoat in order to obtain the desirable bright appearance in the superimposed chromium finish. This chromium surface maintains its bright appearance almost unchanged by weathering. The development of "bright" nickel plating has provided an undercoating in which the buffing operation is unnecessary.

"Bright" nickel is an achievement of major importance in the metal coating field. While methods of obtaining lustrous deposits have been known for some time, it is comparatively recently that processes have been available for the rapid production of bright ductile nickel coatings of any desired thickness. This development has been greatly facilitated by the broader scientific knowledge of electroplating which has been obtained during the past few years.[3]

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[1] Fairhall, Ray and Drinker, *J. Ind. Hygiene*, 6, 307 (1924).

[2] Tay, G. H., *Food Ind.*, 8, 60 (1936).

Heavy coatings of electrodeposited nickel have important uses outside the appearance and corrosion protection fields. In addition to such applications as the reproduction of printing plates, phonograph record plates, and the electroforming of tubes, sheets and other articles, heavy electrodeposits of nickel are increasingly employed in the engineering field in building up and surfacing worn and mismachined parts of all kinds.

Nickel Plating Solutions

The first record of nickel plating was in 1843. As an industry, nickel plating dates from 1870, following the invention in the previous year of the nickel-ammonium sulfate plating solution by Isaac Adams. This "double salt" solution remained in general use until about 1910 when it was gradually displaced for some uses by "single salts," *i.e.*, nickel sulfate.[4] In 1916 a nickel plating bath was proposed by Watts [5] which is typical of the "rapid" nickel solutions used since that time. This bath has a higher metal content, provided in the form of the sulfate and chloride, contains boric acid, and is operated "hot," *i.e.*, at 50-60° C., and at current densities from about 15 to 45 amperes per square foot.

At the present time a large number of bath formulas are employed in nickel plating. These are generally neutral or slightly acid solutions in which the nickel is present principally as the sulfate but which contain sufficient chloride to insure adequate anode dissolution. Boric acid is usually employed to regulate and control acidity and thereby to prevent precipitation of basic compounds at the cathode. Typical of solutions which have been widely used for plating nickel is the following: [6]

	Approximate Normality	Grams/liter	Oz./gal.
Nickel sulfate ($NiSO_4 \cdot 7H_2O$)	1.40	200	27
Nickel chloride ($NiCl_2 \cdot 6H_2O$)	0.40	45	6
Boric acid	0.5 M	30	4

pH=5.3. Temperature 50-60° C. (122-140° F.)
Current density 1.5-5. amp./dm^2 (14-47 amp./sq. ft.)

More recently the trend has been toward the use of higher metallic ion concentrations,[7] higher current densities and higher acidities.[8] In the hot bath it is now common to employ 30 to 35 oz. per gallon of nickel sulfate (with the nickel chloride content given above), current densities as high as 80 amperes per sq. ft., and acidities of the pH range 1.5 to 3.5. Cathodic efficiencies are usually somewhat lower at the higher acidities. Relatively soft deposits are obtained in baths of the above type operated under these conditions. For harder deposits it is customary to employ lower metal concentrations, lower temperatures, current densities and acidities (pH 5.2 to 5.8). Sodium, potassium, ammonium or magnesium sulfates are often added to the plating solution to improve conductivity and throwing power. The sodium salt is said to be the most effective in this respect over a considerable range of acidity.[9] Throwing power is in general better in solutions of high pH than in those of low pH, and is improved by increasing the temperature.[10]

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[3] McKay, R. J., *Metals and Alloys*, 7, 193 (1936).

[4] Hogaboom, G. B., *Inco (International Nickel Co.)*, 13, No. 4, 12 (1936).

[5] Watts, O. P., *Trans. Am. Electrochem. Soc.*, 29, 395 (1916).

[6] Blum, W., and Hogaboom, G. B., "Principles of Electroplating and Electroforming," 2nd ed., New York, McGraw-Hill Book Co., 1930.

[7] Cotton, D. A., *Monthly Rev. Am. Electroplaters' Soc.*, 22, 6, (Dec., 1935).

[8] Phillips, W. M., *Trans. Am. Electrochem. Soc.*, 58, 387 (1930); Griffiths, W. T., (Paper before Electroplaters' and Depositors' Tech. Soc.). *Mond Nickel Co. Bull. L-4.*

Of the metallic impurities which may be found in nickel baths, iron is least objectionable even when present in relatively large amounts; in solutions of moderate acidity it is deposited as a solid solution with nickel. Iron may be oxidized to the ferric condition; and in baths operated in the customary low acidity range ferric iron will be precipitated as ferric hydroxide or basic ferric salts—products which should be filtered out to prevent their inclusion in the nickel deposit. Copper, if present in small amounts, will produce dark spots in nickel coatings. As little as 0.05 per cent zinc may give rise to streaky deposits.[6] Traces of lead may enter nickel plating solutions, being derived from lead-linings, heating coils or from the anodes. It is deposited with the nickel, yielding deposits of reduced grain size which are brittle and have a tendency to peel.[11] Aluminum, while not ordinarily an impurity in nickel salts, tends, if present, to accumulate in the cathode film forming colloidal compounds which give rise to burnt or black deposits.[12] It has long been known that organic contaminants in nickel baths are conducive to brittle deposits. Studies have lately shown that contact of nickel solutions with such materials as wood, cotton and silk may produce hard, brittle deposits usually lustrous in appearance.[13]

Nickel anodes tend to become passive, particularly in sulfate baths. Formerly cast nickel anodes containing several per cent of iron and usually other impurities were commonly used because of their greater solubility. With the growing recognition of the dependence of quality of the electrodeposit upon purity of solution, the use of anodes of higher purity has become prevalent. These anodes consist of rolled or cast metal and may average as high as 99.5 to 99.9 per cent nickel.[14] The uniformity of corrosion of rolled anodes may be improved by suitable annealing.[6] Nickel particles or inclusions produced in the dissolution of the anodes are prevented from reaching the bath by enclosing the anodes in bags made of cotton, glass or wool.

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[9] Harr, R., *Trans. Electrochem. Soc.*, 68, 425 (1935).
[10] Harr, R., *Trans. Electrochem. Soc.*, 64, 249 (1933).
[11] Raub, E., and Wittum, M., *Korr. Metallschutz*, 13, 261 (1937).
[12] O'Sullivan, J. B., *Trans. Faraday Soc.*, 26, 533 (1930).
[13] Hothersall, A. W., and Gardam, G. E., *Met. Ind. (London)*, 50, 609 (1937).
[14] Werner, E., *Metallbörse*, 24, 1466 (1934).

Application of Nickel Plating to Aluminum and Zinc Alloys

Aluminum and its alloys, particularly die-casting alloys, are often plated with nickel, and this is usually followed with a chromium finish. In preparation for nickel plating it is essential that the aluminum or aluminum alloy surface be thoroughly cleaned and that it be roughened somewhat to insure adherence. A suitable surface condition may be obtained by mild sand-blasting and by various etching reagents. Of the latter, a solution of nickel chloride (about $2N$) in normal hydrochloric acid or an acidified solution of ferric chloride [15] may be used for aluminum; for die-cast and sand-cast aluminum alloys a strong acid dip composed of 3 parts by volume of concentrated nitric acid and 1 part of 50-per cent hydrofluoric acid is desirable.[16] Another method of surface preparation for aluminum consists in immersion in dilute hot caustic (pH 10) containing chromates or silicates as inhibitors.[17] Another solution which has been proposed [18] as a preliminary dip is sodium zincate, which upon immersion deposits a superficial film of zinc on the aluminum surface. It is then plated by methods to be described presently for the nickel plating of zinc alloys. Nickel baths high in sulfate or containing citrates are generally employed in plating aluminum.

With the wide use of zinc-base die-castings in the automobile industry in recent years, nickel plating of these alloys has become general. Here again, the chromium finish is used for appearance. Door handles and radiator grills are conspicuous examples of nickel-chromium plated die-castings.

Zinc alloys of this type are polished either over the entire surface or only on the parting lines, usually buffed and then generally degreased with trichlorethylene in a three-stage system involving hot dipping, cold rinsing and a final vapor rinse.[19] All platers use an alkaline cleaner, commonly at 180° F., and in the majority of cases the castings are cathodically treated in such solutions. An acid dip consisting of 5- to 10-per cent hydrochloric acid or 5-per cent sulfuric acid is used to remove alkaline salts or superficial oxide, the work being left in the solution until there is evidence of gas evolution.

Zinc-base die-castings are plated either directly with nickel or with a composite copper-nickel coating. For relatively mild indoor use coatings of 0.0003 inch of nickel are common, while for more severe exposures, particularly for outdoor service, coatings 0.0008 to 0.001 inch in thickness (of which 0.0002 to 0.0003 inch is copper) are used. The solution for

[15] Ballay, M., *Trans. Electrochem. Soc.*, **62**, 91 (1932).

[16] Work, H. K., *Trans. Am. Electrochem. Soc.*, **53**, 361 (1928).

[17] Altmannsberger, K., *Chem. Ztg.*, **55**, 709 (1931).

[18] Fröhlich, W., *Metallbörse*, **24**, 405, 439, 469 (1934).

[19] Anderson, E. A. (N. J. Zinc Co.), *Private Communication*, June 11, 1938. Also, Metal Cleaning and Finish, **10**, 610, 614 (1938).

plating nickel directly is a low nickel-high sodium sulfate solution containing ammonium chloride and buffered in the pH range 4.9 to 5.7 by boric acid. In such a solution the ionization of nickel is repressed to such an extent that the deposition potential of nickel becomes electronegative to that of the alloy. Sodium citrate has been used in place of sodium sulfate to accomplish the same result by the formation of a complex ion which yields a low nickel-ion concentration.

The copper solution used for depositing the copper undercoating in the copper-nickel finish is usually the Rochelle salt-alkaline cyanide bath described in Chapter 10. It is common practice to dip all copper-plated work in dilute sulfuric acid in order to neutralize traces of remaining alkali. Two separate nickel solutions may be employed for heavy nickel coatings. Most platers now use proprietary bright nickel solutions for the deposition of the final nickel coating; otherwise the Watts type bath is used and the deposit color-buffed for brightness.

Nickel coatings on aluminum and zinc-base die-castings have sometimes shown a tendency to peel off or blister under severe atmospheric corrosion if the coating is porous or abraded.

Applications of Heavy Electroplated Coatings

Nickel coatings, because of their superior wear-resisting properties, are used to a considerable extent on electrotypes and to a smaller extent on stereotype plates. They serve as protective coatings, not only in a mechanical sense by resisting wear, but also in a chemical way since they withstand the chemical action of colored ink much better than does copper.[20]

The use of heavy coatings of electroplated nickel on worn machine parts to provide fresh bearing surfaces and shafts which may be re-used [21] has been referred to previously. Similarly, heavy deposits of nickel are plated on articles which are subject to wear or erosion such as, for example, propellers, turbine blades, hydraulic rams, paper machine rolls, etc.

It has been shown [22] that by nickel plating brass articles which are subject to deterioration by season cracking resulting from the combined action of internal tensile stress and a surface corrosive attack, such deterioration can be prevented.

Bright Nickel Plating

The improvements made in the electrodeposition of nickel recently deserve special consideration. The importance of bright, smooth deposits as undercoatings for chromium has been mentioned. Equally promising and of widespread commercial use are bright deposits of sufficient softness to permit forming operations when the plating is applied beforehand to steel strip. Moreover, deposits of this kind may be obtained at current densities as high as 60 amperes per square foot.[3] The ductility of coatings of bright nickel applied by one of the new processes[23] is illustrated in Figure 35.

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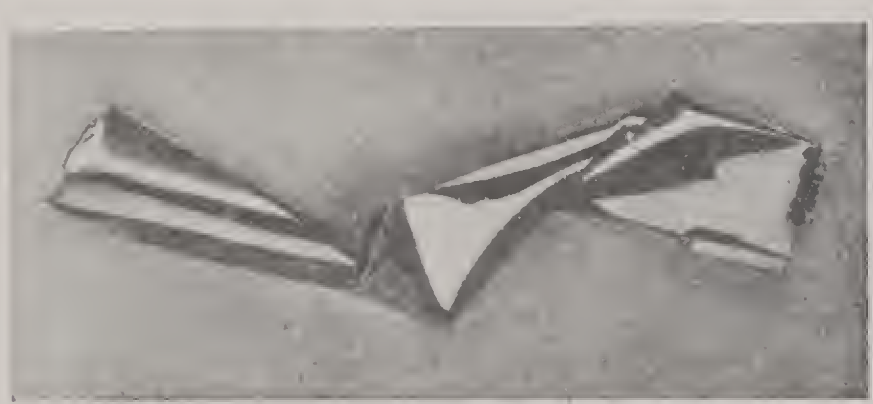
[20] U. S. Bur. Standards, Circular No. 100 (1924).

[21] Bonilla, C. F., *Trans. Electrochem. Soc.*, 71, 263 (1937).

[22] Moore, H., Beckinsale, S., and Mallinson, C. E., *J. Inst. Metals*, 25, 35 (1921).

There are a number of processes for the production of bright nickel deposits.[24] As early as 1905 the use of ethyl nickel sulfate as a brightening agent was proposed in Germany. The presence in the plating bath of small proportions of zinc or cadmium was observed some years ago to produce bright deposits,[25] and colloids have long been known to give lustrous coatings. Glucose, malic acid, and gelatin have been shown to produce a marked improvement in the appearance of the deposits.[26]



Courtesy Hanson-Van Winkle-Munning Co.

Figure 35.—Steel Strip 0.016 Inch. "Bright" Plated with 0.001 In. Nickel. Deposit is Deformed to Illustrate Ductility.

The newer, patented bright nickel plating solutions usually contain nickel sulfate and chloride and boric acid, to which are added in small percentages a brightening agent which may be an aromatic polysulfonic acid derivative, an organic hydroxy-acid or its salt, a complex polyhydric alcohol, a zinc, cadmium or cobalt salt, or combinations of these. For example, one of these solutions[27] proposes the use of one gram per liter of benzyl naphthalene sodium sulfonate; another process[28] specifies 30 grams per liter either of nickel benzol disulfonate or naphthalene trisulfonate. Other processes employ less definite compounds as, for example, the reaction products of sulfuric acid with a terpenic compound,[29] an oleoresin,[30] or with petroleum.[31] Most of these baths employ wetting agents for the purpose of reducing the tendency to pit. Substances such as sodium gluconate, or sulfonated alcohols [32] may be used for this purpose. One of the most promising baths for bright nickel contains cobalt sulfate, nickel formate, and a small amount of formaldehyde.[23] In this process anodes containing 18 per cent cobalt are employed. The deposit obtained is a cobalt-nickel alloy similar in appearance and properties to bright nickel.

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[23] Weisberg, L., and Stoddard, W. B. Jr., U. S. Patent 2,026,718, (Jan. 7, 1936).

[24] For resumé of patented processes of bright nickel plating, see Johnson, L. W., *Met. Ind. (London)*, 50, 281 (1937).

[25] Haring, H. E., *Trans. Am. Electrochem. Soc.*, 46, 107 (1924).

[26] Stout, L. E., *Monthly Rev. Am. Electroplaters' Soc.*, 23, May (1936), p. 25; Anon., *Metallwaren. Ind. Galv. Tech.*, 33, March 1, (1935).

[27] Lutz, G., and Westbrook, L. R., U. S. Patent 1,818,229, (Aug. 11, 1931).

[28] Schlötter, M., U. S. Patent 1,972,693, (Sept. 4, 1934).

[29] British Patent 436,042, (Nov. 3, 1934).

[30] Pine, P. R., U. S. Patent 2,029,386, (Feb. 4, 1936).

[31] British Patent 437,224, (Nov. 3, 1934).

The brilliance of nickel deposits from these baths is said to be due to fineness of grain size, which is of the order of the wave-length of light, and to the orientation of the crystals in the surface. Formerly, bright deposits were usually brittle and given to peeling. The present product, while harder than ordinary nickel deposits having the matte appearance, is reasonably ductile and is adherent if plated upon a suitably prepared base.

"Nickel-Clad" Steel

Nickel-clad sheet steel is made on a commercial scale.[33] The product is usually from ¼ to ½ inch in thickness with a layer of nickel on one side comprising from 5 to 20 per cent of the weight of the entire sheet. This represents in the half-inch stock about 0.45 inch of steel and about 0.05 inch of nickel. The product is supplied in standard claddings of 5, 10, 15 and 20 per cent nickel. The nickel coating may be bonded to both surfaces of steel sheet. "Inconel," an alloy of approximately 78 to 80 per cent nickel, 12 to 14 per cent chromium and 6 to 8 per cent iron, may be employed instead of nickel as a cladding material.[34]

In making nickel-clad steel relatively heavy layers of steel and nickel are placed in intimate contact, heated to a temperature of about 2200° F. (1200° C.) and rolled to the finished plate. Inconel-clad steel is fabricated in an analogous manner. The bonding of the two metals in the case of the nickel-clad product is accomplished by superficial alloying at the steel-nickel interface. It is essential that the nickel surface be continuous, that all joints be strong and that all sheared edges be covered. Nickel-clad steel is finding useful applications in the chemical equipment field, particularly in processes dealing with brines, alkalies, acids, soaps, dyes, etc. Inconel-clad steel is suitable for equipment to be used in the brewing, distilling, textile, tanning and pharmaceutical industries.

Corrosion Resistance of Nickel Coatings

The protective value of nickel coatings is dependent largely upon their continuity. They function in most cases merely as physical barriers for the exclusion of air and moisture and do not at perforations in the coating afford electrochemical protection to exposed iron or steel. As in the case of tin-plate, pores in nickel coatings soon manifest themselves by the appearance of iron rust at those points.

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[32] British Patent 438,412, (May 13, 1935).

[33] Humpton, W. G., Huston, F. P., and McKay, R. J., *Mining Met.*, 12, 90 (1931); Huston, F. P., *Internat. Nickel Co. Bull. T-4* (Sept. 1938).

[34] Theisinger, W. G., and Huston, F. P., "Metals Handbook," American Society for Metals, 1938.

Nickel exposed to air low in relative humidity and sulfurous gases remains bright in appearance for long periods of time. An invisible film of corrosion products forms under these circumstances as is proven by gains in weight of exposed test specimens. Figure 36,[35] illustrates with curves the weight increments with time of exposure of pure nickel specimens

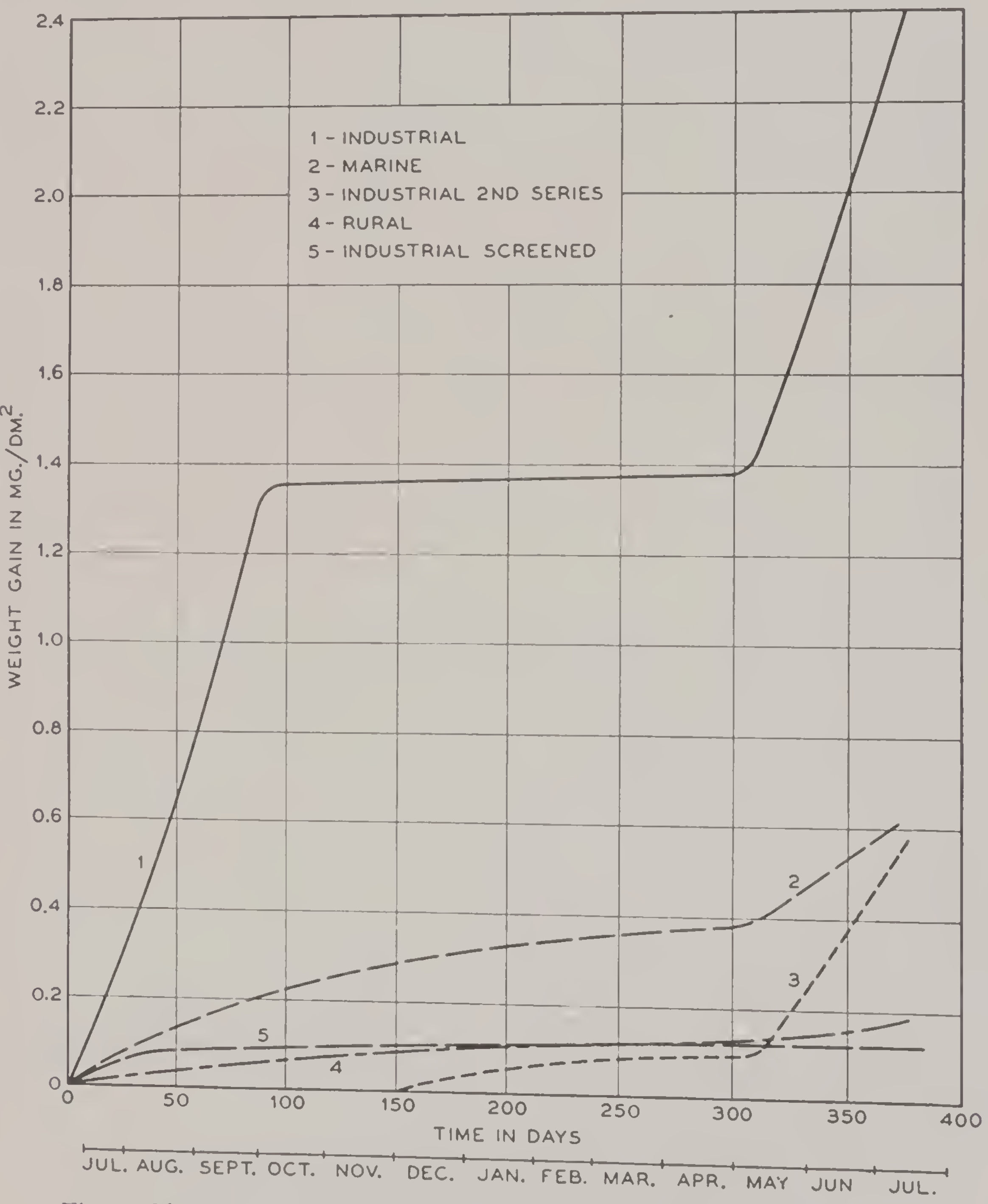

Figure 36.—Rate of Tarnish of Nickel in Various Indoor Atmospheres.

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[35] Experiments by Messrs. W. E. Campbell and U. B. Thomas, Bell Telephone Laboratories. New York, N. Y.

placed indoors in heavy industrial (New York City), marine (Asbury Park, N. J.) and rural (Rockaway, N. J.) locations. It is seen that with the exception of the industrial station, the weight gains during the first 300 days were less than correspond to the thickness of visible films. It is of interest to observe in this figure that a similar result was obtained at the industrial location provided the nickel specimens were exposed in a "squirrel cage" surrounded by a muslin screen. The marked retardation of corrosion obtained by the use of muslin screens has been previously reported in studies on iron,[36] in which it was shown that rusting of specimens behind muslin was prevented, although a slight increase in weight occurred. The existence of an oxide film on nickel exposed to air of low relative humidity has been detected also by optical methods and it has been shown that this film is soluble in sulfuric acid.[37]

In air at relative humidities in excess of approximately 70 per cent[38] and containing sulfur dioxide in the quantities prevailing in industrial atmospheres (0.75-2.0 parts per million), nickel becomes covered with a cloudy film—a process known as "fogging." In the early stages the film may be readily wiped off, revealing the underlying metal surface to be still bright in appearance. Later, however, the fogging cannot be removed without abrading the metal. The weight-increment-time results obtained in the fogging of nickel are illustrated in Figure 36 by the curve for the specimens exposed at the industrial station. Fogging occurred only during the humid summer months since specimens set in December remained bright until May and then became cloudy in appearance. It should be pointed out that protective nickel coatings to be used in the atmosphere are now universally coated with a superficial layer of chromium which obviates fogging.

The mechanism of fogging apparently consists in the catalytic oxidation of sulfur dioxide to sulfur trioxide,[38] followed by corrosion of the nickel surface to nickel sulfate in the resulting film of sulfuric acid. That a catalytic process is involved is indicated by the fact that previous exposure of the fresh nickel surface to hydrogen sulfide markedly inhibits fogging—a reaction suggestive of the well-known poisoning effect of hydrogen sulfide on catalytically active surfaces. It is of interest to note that the rate of fogging is approximately halved when light is completely excluded. Chemical analysis of "fog" films formed in normal atmosphere has given the following results:[38]

After 21 days' exposure $NiSO_4 \cdot 0.26\ H_2SO_4$
After 88 days' exposure $NiSO_4 \cdot 0.33\ Ni(OH)_2$

Several tests have been made of the resistance of nickel to outdoor atmospheres. The results obtained by the Atmospheric Research Committee of the British Non-Ferrous Metals Research Association, after an exposure of one year in various atmospheres, are given in Table 19. The values reported are in terms of average thickness of corroded layer and are calculated from the experimental results for loss in weight of plate and wire specimens and for increase in electrical resistance of wire specimens.[39]

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[36] Vernon, W. H. J., *Trans. Faraday Soc.*, 23, 159 (1927).
[37] Tronstad, L., *Z. physikal. Chem.*, 142, [A] 241 (1929).
[38] Vernon, W. H. J., *J. Inst. Metals*, 48, 121 (1932).

The greater severity of corrosion in the sulfur-bearing urban and industrial atmospheres is apparent. As in the case of zinc, marine atmospheres corrode nickel at a rate which is intermediate between that experienced in rural and industrial locations. The relatively greater intensity of attack shown for the electrical resistance method of test may be attributed to the greater circulation of air around wire specimens as compared with plate specimens, and also to the greater sensitivity of this method to penetration of attack along grain boundaries.

Table 19.—Average Thickness of Corroded Layer of Nickel Specimens Expressed in Millionths of an Inch Per Annum.

Exposure	Cardington (Rural)	Bournville (Suburban)	Wakefield (Industrial)	Birmingham (Urban)	Southport (Marine)
Stevenson Screen Wt. increment (wire)	64	97	227	245	141
Electrical Resistance (wire)	168	274	560	564	325
Weight-loss (plates)	45	96	218	230	111

Nickel is included in the comprehensive atmospheric corrosion test conducted by Committee B-3 of the American Society for Testing Materials, the results of which at the end of six years of exposure are given in Table 20.[40]

Here again nickel is seen to be corroded markedly more in the industrial atmospheres than at either rural or marine stations whether the deterioration is expressed as change of weight or loss in tensile strength. The urban air of Rochester, New York, and the sea air of the northern marine location, Sandy Hook, N. J. are of similar severity, while La Jolla, on the California coast, and Key West, Florida, are similar in mildness. Finally, it will be noted that the arid pure air of Phoenix, Arizona, is practically without action on nickel.

The foregoing discussion of the atmospheric corrodibility of nickel is applicable to nickel coatings of sufficient thickness to be practically pore-free and to provide thereby a continuous envelope of nickel about the base metal, iron, steel or brass, the protection of which is sought. Commercial nickel coatings are never entirely non-porous, although in recent years there has been a definite trend toward the use of thicker and therefore less porous coatings. Until a few years ago, the maximum thickness of commercial nickel coatings averaged 0.0002 inch, whereas at the present time thicknesses of 0.001 to 0.002 inch are commonly specified.[41] Incidentally, the

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[39] Hudson, J. C., *Trans. Faraday Soc.*, 25, 233 (1929).
[40] Finkeldey, W. H., *Proc. Am. Soc. Testing Materials*, Part 1, p. 38, (1938).
[41] Hogaboom, G. B., *Inco (Internat. Nickel Co.)*, 13, No. 4, 12 (1936).

Table 20.—Atmospheric Corrosion of Nickel.

Location	Original Weight	Change in weight, grams			Tensile Properties After 6 yrs.		% Change in Tensile Properties		Remarks
		1 yr.	3 yrs.	6 yrs.	Tensile Strength	Elongation (%)	Tensile Strength	Elongation (%)	
Pittsburgh No. 1	560.76 564.43	−3.90 −3.86	−10.82 −10.71	−23.05 −22.79	68,700	36.7	−5.9 (*1.3*)	−0.3 (*1.8*)	Heavy dark film.
Altoona No. 2	565.49 565.60	−3.83 −3.95	−11.76 −12.04	−24.86 −25.48	67,300	36.6	−7.8 (*1.3*)	−0.5 (*1.4*)	Heavy dark film with patches of slight scale.
New York City No. 4	561.82 565.53	−5.01 −5.07	−12.48 −12.58	−24.46 −24.45	67,600	36.3	−7.4 (*1.4*)	−1.4 (*1.2*)	Smooth heavy film with slightly mottled appearance.
Rochester No. 6	561.22 566.87	−0.53 −0.54	−2.03 −2.06	−5.52 −5.76	71,500	36.5	−2.0 (*1.4*)	−0.8 (*1.9*)	Smooth mottled film.
Sandy Hook No. 5	561.51 562.28	−0.74 −0.74	−2.36 −2.39	−5.10 −5.14	72,000	37.0	−1.4 (*1.2*)	+0.5 (*2.3*)	Smooth slate-colored film.
Key West No. 7	564.13 559.16	−0.14 −0.14	−0.41 −0.41	−0.75 −0.75	72,950	36.7	−0.1 (*1.2*)	−0.3 (*1.8*)	Very light film, metallic luster.
La Jolla No. 9	563.82 563.36	+0.08 +0.10	−0.19 −0.19	−0.53 −0.57	72,900	36.3	−0.1 (*1.3*)	−1.4 (*2.6*)	Slight speckling of powdery scale, underlying tarnish.
State College No. 3	566.06 562.88	−0.12 −0.12	−0.39 −0.38	−0.97 −0.98	73,650	37.0	+0.9 (*1.2*)	+0.5 (*0.8*)	Very slight tarnish.
Phoenix No. 8	564.94 561.31	0.00 0.00	−0.06 −0.06	−0.09 −0.10	72,800	35.9	−0.3 (*1.1*)	−2.4 (*1.0*)	Slight tarnish.

Note: Italics denote maximum per cent difference due to chance.

domestic consumption of nickel anodes increased from 2,500,000 pounds in 1926 to 9,000,000 pounds in 1937, owing to the increased use of nickel in the automobile industry as well as the trend toward increased thickness of coating. For automobile parts nickel undercoatings for chromium plate are generally 0.001 inch in thickness, and may be as much as 0.0015 inch on bumpers.

The relation of porosity to coating thickness for nickel coatings reported in recent investigations is given in Figure 37.[3] These coatings are probably somewhat superior to the usual commercial product of this range of coating thickness, but the data indicate the advantage which has been obtained in going to heavier coatings. While coatings 0.0015 inch in thickness are practically non-porous in character, it is seldom in commercial practice that this thickness is obtained in the recessed areas of articles of irregular shape. The interposition of a thin coat of copper between two coats of nickel, though uncommon in American practice, is a practical method of reducing the number of pits in deposits of ordinary commercial thickness.[42]

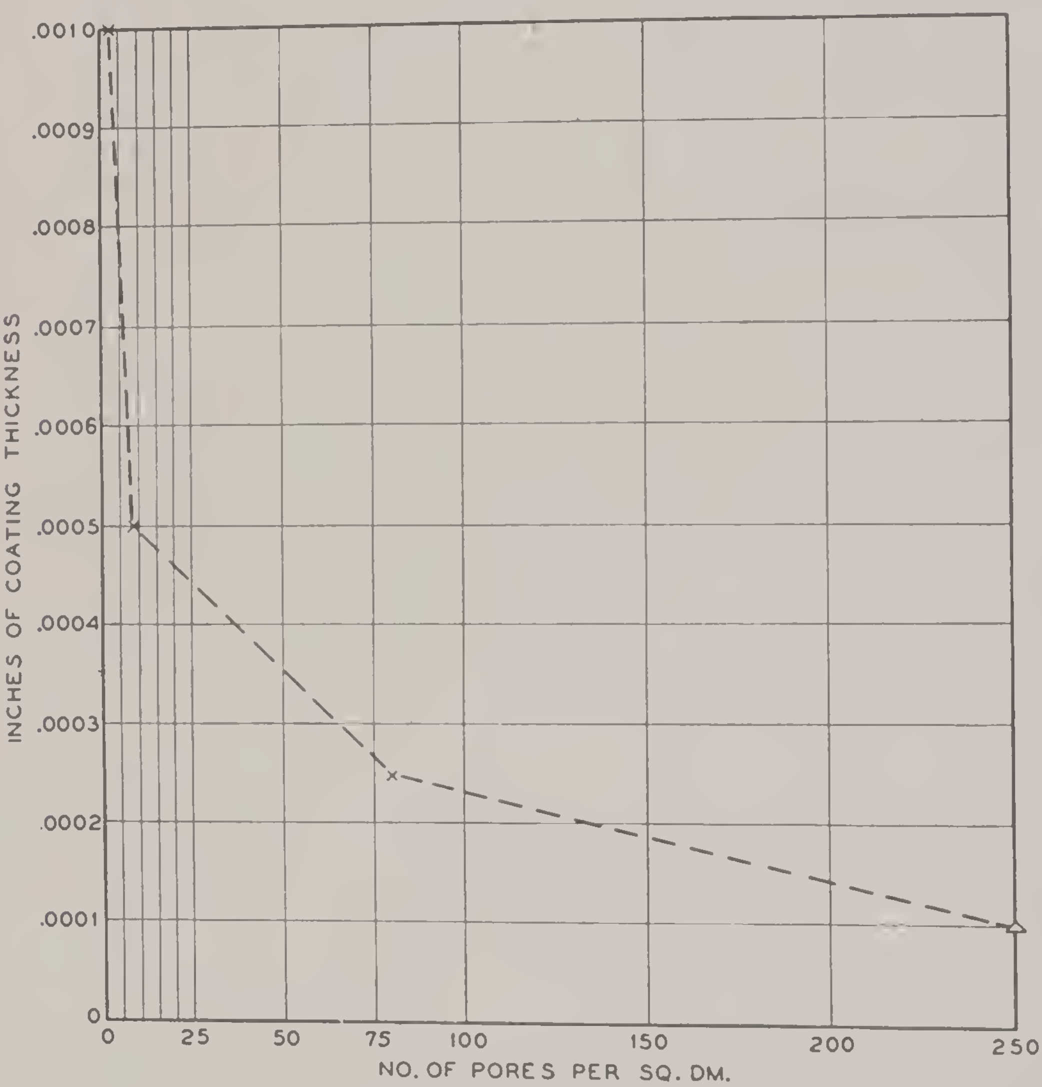

Figure 37.—Relation of Porosity to Coating Thickness for Nickel Coatings.[3]

Tests have indicated that electrodeposited nickel coatings 0.002 inch in thickness are equivalent in protective value to sprayed nickel coatings tenfold greater in thickness.[43]

The causes of porosity in nickel coatings are numerous and complicated and have been the subject of considerable study. Hydrogen is discharged in nickel plating, particularly in the early stages of deposition, and it has long been assumed that bubbles of this gas or of air have by adhering to the cathode given rise to pores. It has been suggested [44] that an accumulation of colloidal nickel compounds (probably hydrates) near the cathode is a factor favoring retention of hydrogen bubbles upon the cathode surface. It has lately been emphasized,[45] however, that gas bubbles are an incidental rather than a primary cause of porosity. Imperfections or impurities in the basis metal surface which are usually the foci of hydrogen evolution are areas which in themselves are not readily covered with the electrodeposit.

Among the principal causes of pitting are finely divided solid matter in suspension in the solution, foreign matter such as slag inclusions, buffing compounds in the surface of the steel, and a roughened condition of the surface. The suspended matter in the solution may be derived from anode slimes, precipitated basic compounds of iron, air-borne dust, calcium sulfate (from hard water used in preparation of solutions), lead sulfate (from lead linings of tanks), and finally, particles such as carbides, silica, etc., which are loosened in the surface of the basis metal in its preparation for electroplating. The marked reduction in porosity of nickel coatings obtained by the removal of solid particles by filtration of the plating solution is given in Table 21. Filtration (Series F) was accomplished by means of suction through a Büchner funnel using a fine filter paper. In one case (Series FF) filtration in this manner was preceded by boiling the solution with freshly precipitated nickel hydroxide. The specimens employed in this test were curved strips of steel.

Table 21.—The Effect of Filtration on Porosity.[45]

Condition of Solution		Average Thickness of Deposit		No. of Specimens Tested	Average Porosity (No. pores per dm.^{2})	
		(in.)	(mm.)		Concave Sides	Convex Sides
Not filtered	Series NF	0.001	0.025	5	30	9
Carefully filtered	Series F			3	6.2	0.9
Not filtered	Series NF	0.0006	0.015	5	86	51
Carefully filtered	Series F			3	10	2.6
Not filtered	Series NF	0.0002	0.005	5	230	152
Carefully filtered	Series F			3	113	66
Specially filtered	Series FF			9	32	25

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[42] Cymboliste, M., *Trans. Electrochem. Soc.*, 70, 379 (1936).

[43] LaQue, F. L., *Internat. Nickel Co. Bull. T-13*, Dec., 1937.

[44] Macnaughton, D. J., Gardam, G. E., and Hammond, R. A. F., *Trans. Faraday Soc.*, 29, 729 (1933).

[45] Hothersall, A. W., and Hammond, R. A. F., *Trans. Electrochem. Soc., Preprint*, 73, 449 (1938). This excellent analysis of the causes of porosity is the principal source of the information given in the following paragraph.

As already mentioned the physical state of the cathode surface has an important bearing upon pitting in thin nickel deposits. Sandblasting or file-scratching of a polished steel surface prior to the deposition of coatings 0.00006 to 0.0002 inch in thickness has been shown to produce very marked increases in porosity. The fine-grained surface produced by etching steel anodically in concentrated phosphoric acid is more suitable than the relatively coarse-grained surface obtained in dilute sulfuric acid for the production of nickel coats of low porosity.[46]

The ordinary type of pores in nickel coatings which have been under discussion in the preceding chapters consist in microscopic channels extending through the coating to the basis metal. To be distinguished from pores are defects known as pits; these are craters of varying depth which may perforate the coating. While many of the conditions responsible for porosity may also give rise to pitting, a careful investigation of the matter has led to the conclusion [44] that pitting is associated with the presence of flocculated basic matter at the cathode surface. The prevention of pitting, then, involves such measures as filtration and the removal of organic impurities from the bath by oxidation with hydrogen peroxide, chlorine [47] or potassium permanganate.[48] It has been shown also, that pitting in baths of low acidity may be reduced by the introduction of sodium or potassium salts, and this result has been attributed to the stabilizing effect of alkali ions in preventing the flocculation of basic colloids.

Under certain plating conditions another type of defect, known as a blister pit, may appear. As the name implies, these are larger in size than ordinary pits and resemble blisters in appearance. Blister pits are probably due to small adherent gas bubbles which are gradually plated over during the deposition of the coating. There is evidence that in the formation of blister pits flocculent basic salts of relatively high electrical conductivity become attached to the surface of gas bubbles and that the electrodeposit is subsequently plated upon or grows over these colloid-coated bubbles.[49]

The practical importance of these considerations of the nature and causes of porosity and pitting lies in the possibility that a fuller knowledge of the factors involved will make possible the commercial production of nickel coatings of higher quality. An experimental study has shown that, by eliminating suspended matter from the solution and using specially prepared electrolytic iron or finely machined mild steel rod as basis metal, it is possible to obtain pore-free nickel deposits less than 0.0001 inch (0.0025 mm.) in thickness.[45] In view of the progress made in the field of electroplating in recent years it is not too much to expect that coatings of this quality will be obtained on a commercial basis.

It is well established, and is implied in the foregoing discussion, that the protective value of commercial nickel coatings in the atmosphere is a function of their porosity and hence, at the present time, of their thickness. For instance, in the exposure tests conducted at the National Bureau of Standards in coöperation with the American Electroplaters' Society and the American Society for Testing Materials it was found that the thickness of the nickel layer is more important than any other factor.[50] The results obtained in this test at the end of 18 months of exposure are recorded in Table 22. The composition of the plating bath employed is that given earlier in the present chapter under the discussion of nickel plating solutions. The bath was operated at 35° C. at a current density of 2 amperes per sq. dm. in the procedure designated as "standard." Sets 4 and 7 were plated in this bath at 60° C., and 4 amperes per sq. dm. For Set 4 the pH value of the solution was 5.3 and for Set 7 the pH was 2.5.

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[46] Burns, R. M., and Warner, C. W., U. S. Patent 1,658,222, (Feb. 7, 1928).

[47] Dorsey, F. M., *Ind. Eng. Chem.*, 20, 1094 (1928).

[48] Macnaughton, D. J., and Hothersall, A. W., *Trans. Faraday Soc.*, 26, 163 (1930).

[49] Cymboliste, M., and Salauze, J., *Trans. Electrochem. Soc.*, 71, 233 (1937).

Table 22.—Effect of Thickness of Nickel and Conditions of Deposition on Protective Value of Coatirgs.

Exposure 18 months. Per cent scores (see below).

Set No.	Procedure	Thickness inches × 1000	Key West (Marine)	New York City (Industrial)	Pittsburgh (Industrial)	Sandy Hook (Marine)	State College (Rural)	Washington (Suburban)	Average (6)	Marine Average (K.W., S.H.)	Industrial Average (N.Y., P.)	Suburban Average (S.C., W.)
52	Standard	0.25	10	17	8	10	31	35	19	10	13	33
5	Standard	0.50	25	30	20	27	70	82	42	26	25	76
1	Standard	1.00	67	67	36	62	87	86	68	65	52	87
2	Cath. pickle	1.00	54	67	36	64	91	87	68	59	52	89
3	Anode pickle	1.00	76	66	36	68	89	87	70	72	51	88
5	High temp., high pH	1.00	79	62	36	61	86	87	69	70	49	87
7	High temp., low pH	1.00	54	61	34	62	77	83	62	58	48	80
51	Std., not buffed	1.00	31	61	37	56	87	91	61	44	49	89
	Average (with 1.0)	1.00	60	64	36	62	86	87	66	61	50	87
6	Standard	2.00	79	86	52	79	96	94	81	79	69	95

Method of rating specimens:

Surface rusted (Per cent)	Rating	Percentage score
0	5	100
0–5	4	80
5–10	3	60
10–20	2	40
20–50	1	20
50–100	0	0

It is apparent from an inspection of the results in Table 22, which are based on over 100,000 individual ratings of specimens, that coatings with a thickness of only 0.00025 in. (0.006 mm.) afford very little protection to steel in exposures to outdoor atmosphere. Twice this thickness of coating, 0.0005 in. (0.013 mm.) is serviceable only in the mild atmospheres of rural or suburban localities, while coatings of 0.001 in. (0.025 mm.) are satisfactory except in highly industrial atmospheres. It will be seen that variation in the manner of electroplating is without any appreciable effect upon the protective value of the deposit.

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[50] Blum, W., Strausser, P. W. C., and Brenner, A., *J. Res. Nat. Bur. Stds.*, **13**, 331 (1934).

Accelerated corrosion tests[51] and also outdoor exposure tests[52] have indicated that the corrosion resistance of a nickel coating deposited as a single layer is less than the resistance of a coating containing the same amount of nickel in the form of two layers with a film of copper sandwiched between. More recently the influence of a layer of copper on the protective value of nickel coatings was studied more extensively[50] by including composite nickel-copper-nickel coatings in the coöperative exposure test which has been described in the two previous paragraphs. The per cent variation in scores from those in Table 22 for pure nickel deposits of the same total thickness is given in Table 23. The copper layer was deposited from both cyanide and acid copper solutions without any significant difference in behavior being detectable. These results appear to be conclusive.

Table 23.—Effect of an Intermediate Layer of Copper on the Protective Value of Nickel Coatings.[50]

Per cent variation in scores from those of pure nickel deposits of the same total thickness.

Thickness (inches × 1000)	Key West	New York	Pittsburgh	Sandy Hook	State College	Washington	Average (6)	Marine Average	Industrial Average	Suburban Average
0.25	−7	+2	−2	−5	−18	−18	−8	−6	0	−18
0.50	−18	+15	−3	−8	+5	+4	0	−13	+6	+5
1.00 (Avg. of 9)	−42	+11	−13	−10	+2	+6	−8	−25	0	+4
2.00	−19	+8	−17	−1	+4	+4	−3	−10	−4	+4
Average	−21	+9	−9	−6	−2	−1	−5	−14	0	−1

It will be seen from Table 23 that the presence of copper is detrimental in very thin coatings in all locations and that corrosion is accelerated by copper in composite coatings of all thicknesses included in the test when exposed to marine or highly industrial atmospheres. On the other hand, the beneficial effect of copper is confirmed for the heavier coatings in rural, suburban and moderately industrial localities. It was found in this investigation that buffing of the copper layer improved somewhat the performance of the coating.

A preliminary layer of zinc or cadmium is sometimes used in nickel plating. As a rule, however, such coatings do not retain their bright metallic luster as well as do nickel coatings alone when exposed to corrosive conditions owing to a staining or filming of the surface by zinc or cadmium corrosion products. The protective value of composite zinc-nickel coatings is less than that of either metal alone, and cadmium under nickel has very little effect.[50]

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[51] Baker, E. M., *J. Soc. Auto. Eng.*, 14, 127 (1924).

[52] Thomas, C. T., and Blum, W., *Trans. Am. Electrochem. Soc.*, 48, 69 (1925); 52, 271 (1927).

Microstructure of Electrodeposited Nickel Coatings

The microstructure of electrodeposited nickel is similar to that of other electroplated coatings, although the grain size is usually much smaller, particularly in deposits obtained at low pH from solutions consisting entirely or in part of nickel chloride. Deposits from nickel sulfate baths of low pH, on the other hand, are somewhat coarse-grained, soft and ductile.[53] Raising the pH value (lowering the acidity) of the plating solution tends to refine the grain size and increase the hardness of the deposit. It has been observed, further, that alkali metal ions, and particularly ammonium ions, tend to harden nickel deposits.[54] At low temperatures and low current densities, the presence of chlorides in the plating solution has long been known by general experience to produce soft deposits; yet it has been shown that at high current densities and high temperatures the presence of chloride leads to hard deposits.[53] It is evident that nickel deposits of a wide range of hardness can be obtained by the proper adjustment of the bath and conditions of operation. A comparison of the Brinell hardness range of nickel and other electrodeposited metals is shown in Figure 38.[55]

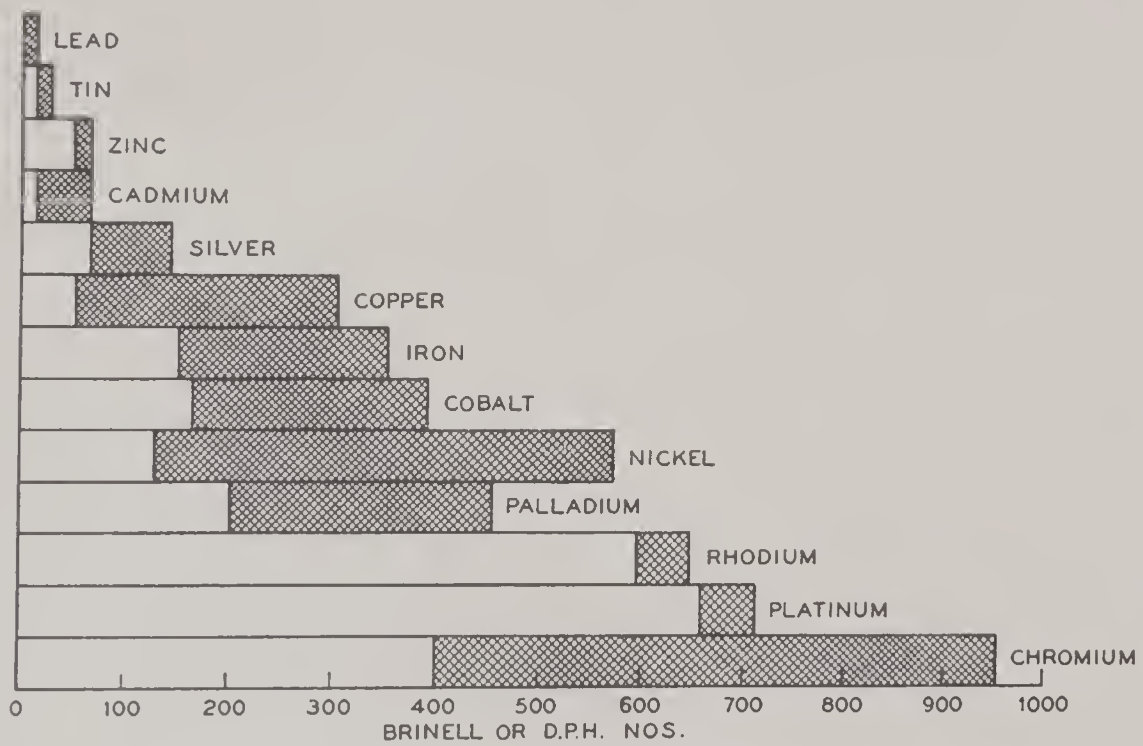

Figure 38.—Brinell Hardness Range of Various Electrodeposited Coatings.

Soft electrodeposited nickel possesses a pronounced fibrous structure with the grains elongated in the direction perpendicular to the surface of the base. This is shown in Figure 39[56] for a deposit of the hardness range

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[53] Blum, W., and Kasper, C., *Trans. Faraday Soc.*, 31, 1203 (1935).

[54] Macnaughton, D. J., and Hothersall, A. W., *Trans. Faraday Soc.*, 31, 1168 (1935).

[55] Hothersall, A. W., *Met. Ind. (London)*, 48, 115 (1936).

[56] Wesley, W. A., *Monthly Rev. Am. Electroplaters' Soc.*, (August, 1938).

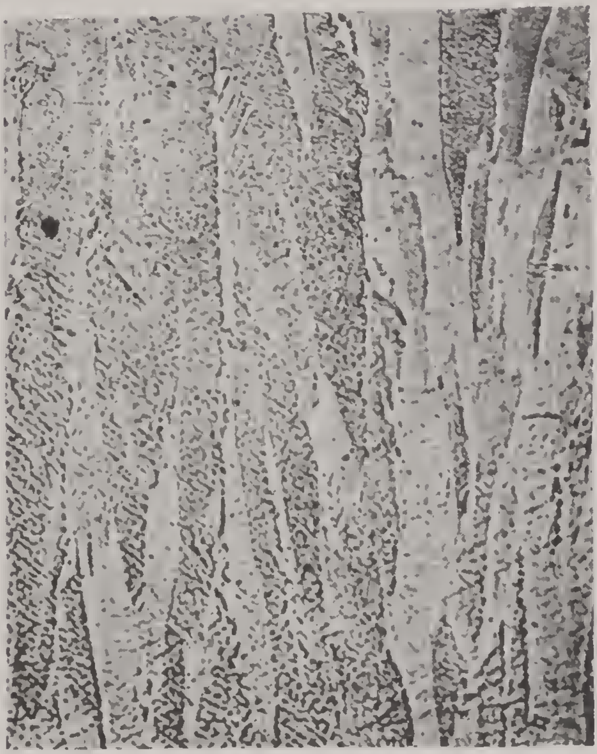

Figure 39.—Structures of Soft Electrodeposited Nickel.[56] Hardness Range 140-160 Vickers (×500).

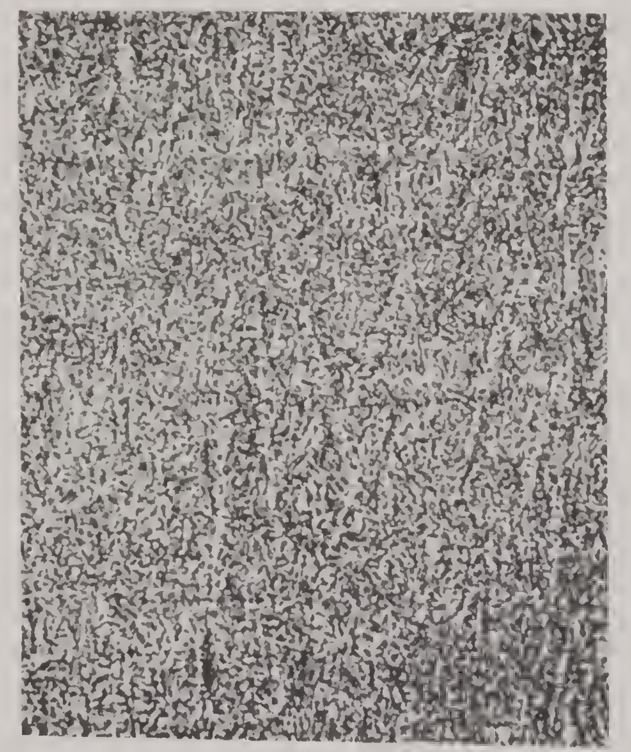

Figure 40.—Structure of Moderately Hard Electrodeposited Nickel.[56] (×500) Hardness: 230 Vickers.

140-160 on the Vickers scale obtained from the warm Watts type bath. Figure 40 illustrates the refinement in grain structure of a moderately hard nickel electrodeposit, and Figure 41 the structure, so far as it can be revealed, of a very hard deposit testing 350-400 in Vickers hardness. In the latter case the grain size is practically sub-microscopic, and in this and the moderately hard deposit the crystals were observed, by x-ray examination, to be oriented in a random fashion.

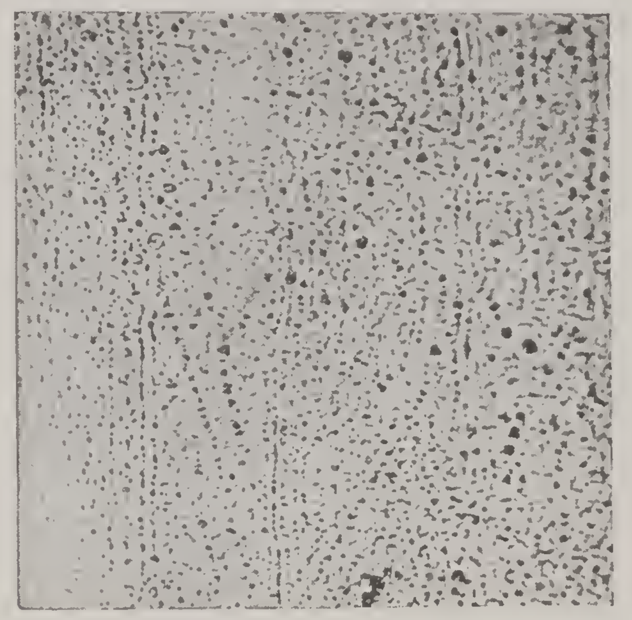

Figure 41.—Structure of Very Hard Electrodeposited Nickel.[56] 350-400 Vickers Hardness. (×500)

The relation of the structure and hardness of nickel deposits to bath composition and operation is still obscure. It has been suggested that the cause of small grain-size and high hardness obtained in solutions of high pH values is due to the interference with crystal growth exerted by colloidal basic nickel compounds.[44] While the Brinell hardness of ordinary nickel deposits may vary from 125 to 400, a hardness of 550 may be obtained by the addition of organic colloids to the plating bath.[54]

Related to structure of deposit is the tendency of certain hard, brittle nickel deposits to peel from the basis metal and curl in tight rolls. This tendency is a factor of importance affecting the adherence of the coating. Apparently such coatings are deposited in a highly stressed condition. It has been demonstrated, for example, that a tensile stress as high as 43,000 pounds per square inch may exist in a nickel coating which, being deposited on one side of a steel ruler, caused the ruler to bend into a bow, the coating being on the concave side.[57] The fact that the tension may be reduced by annealing at low temperatures has suggested that the phenomenon may be due to the deposition of hydrogen in the coating. Coatings which are very highly stressed are usually detected before they are put into service. Such coatings are usually more prone to failure under corrosive conditions than are similar ones not so stressed. Any corrosion between coating and base originating in pores or pinholes in the coating may serve to initiate peeling of the coat.

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[57] Stoney, G. G., *Proc. Roy. Soc.*, 82, (A) 172 (1909).

CHROMIUM COATINGS

Historical

The electrodeposition of chromium[58] was reported in 1854 by the German chemist Bunsen, better known as the inventor of the gas burner which bears his name. However, Geuther (1856) appears to have been the first to deposit the metal from a chromic acid bath. The chromic acid used in the experiments was precipitated from potassium dichromate with sulfuric acid and unquestionably contained a small percentage of sulfate. Geuther obtained "a coherent grayish-white coating with a metallic luster."

Sporadic and frequently unsuccessful attempts were made to repeat Geuther's experiments. It was not until 1905 that Carveth and Curry[59] explained the failures as being due to inadequate current densities, recognized the fact that the sulfate invariably present as an impurity is an essential feature of the bath, and advocated its intentional addition (preferably as sulfuric acid) in proportions up to one per cent. Interest was stimulated by this work and investigations became more frequent and more successful. Various sulfates and a few other salts and acids were substituted for sulfuric acid. Sargent[60] (1920) preferred chromic sulfate to sulfuric acid. Schwartz[61] (1923) employed chromium anodes with "Sargent's solution." It is interesting to note that most of the chromic acid baths studied since Geuther are identical in composition with the bath almost universally employed in present practice.

The slow progress made in the development of chromium plating can be attributed in large part to the little-recognized fact that bright chromium plate, which is now so widely applied, was virtually unknown and the type of deposit usually obtained was not particularly desirable. Investigators were more interested in electrowinning and electrorefining chromium than in electroplating it; and in order to secure maximum efficiency of metal deposition they usually employed high current densities and cold solutions, often chilled with ice. In consequence, the deposits were usually dull and rough, not unlike electrolytic zinc in appearance, and because of their extreme hardness were quite unsuitable for finishing operations.

In 1924, Haring[62] succeeded in consistently depositing a smooth, bright chromium plate with a mirror-like surface which required no buffing. He applied this coating to the intaglio plates used for printing money and stamps at the United States Bureau of Engraving and Printing. This first successful application of chromium plating was not due to any novelty insofar as the plating solution was concerned, but to discovery of the fact that bright chromium can be deposited consistently from the chromic acid bath provided that the current density is carefully maintained within relatively narrow limits, which are determined not only by the bath temperature but also by *the nature of the basis metal.* Since this time, the application of chromium plating has become widespread, and chromium plating practice has changed but little.[58] An extensive patent literature on the subject appeared during the early years of commercial development.[63] Perhaps the best known patent was that granted to Fink in 1926.[64]

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[58] For an excellent account of the history, theory and practice of chromium plating see Haring, H. E., and Barrows, W. P., *Bur. Standards Tech. Paper*, 346, June 10, 1927. Extensive use is made of this article in the present discussion.

[59] Carveth, H. R., and Curry, B. E., *J. Phy. Chem.*, 9, 353 (1905); also *Trans. Am. Electrochem. Soc.*, 7, 115 (1905).

[60] Sargent, G. J., *Trans. Am. Electrochem. Soc.*, 37, 479 (1920).

[61] Schwartz, K. W., *Trans. Am. Electrochem. Soc.*, 44, 451 (1923).

[62] Haring, H. E., *Chem. and Met. Eng.*, 32, 692, 756 (1925).

The principal applications of chromium plating are to plumbing fixtures and automobile parts where a permanently lustrous finish is desired, and to printing plates, tools or machine parts subject to wear where a high degree of hardness is required. For articles which must be used at elevated temperatures, such as flat irons, chromium plating is superior to other metals. All these uses are now well known and established. In the thickness range in which it is generally applied, chromium plate affords but small protection against corrosion.

The high reflectivity of chromium has led to the use of chromium plating for reflectors for locomotive headlights and other similar applications. Although the reflecting power of polished chromium is considerably less than that of polished silver (70 per cent for $\lambda = 0.579\ \mu$ as compared with 93 per cent for silver under the same conditions), the ability of chromium to remain untarnished has led to its use for this purpose. More recently aluminum oxidized by a special process has become a competitor of chromium plating as a reflecting surface.

Theory and Practice of Chromium Plating

Extensive studies have been made in recent years of chromium plating solutions and their operation. Chromium deposits may be obtained from solutions of a variety of chromium salts [65] and also from chromic acid solutions containing small amounts of anions other than sulfates, *e.g.*, fluoride [66] and fluosilicate. It was found early in the industrial development of chromium plating, however, that the chromic acid-sulfate bath gave the most consistent and dependable results. This bath is now used almost universally in commercial practice. The simplest formula for this bath for general purposes is as follows: [6]

Acid		g./1	oz./gal.
Chromic (as CrO_3)	2.5 *M*	250	33
Sulfuric	0.025 *N* to 0.05 *N*	1.25 to 2.5	0.17 to 0.33

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[63] Schneidewind, R., *Univ. Mich. Eng. Research Bull. No. 8*, (Nov., 1927).

[64] Fink, C. G., U. S. Patent 1,581,188, (April 20, 1926).

[65] Britton, H. T., and Westcott, O. B., *Trans. Faraday Soc.*, 27, 809 (1931); 28, 627 (1932).

[66] Hambuechen, C., U. S. Patent 1,544,451, (1925).

Somewhat higher chromic acid concentrations may be used for special purposes. Baths of the above compositions may be operated at a temperature of 45 to 55° C. (113 to 131° F.) and at an average current density of 10 to 30 amperes per square decimeter (93 to 280 amp./sq. ft.). Lead or steel anodes are generally employed, the former being preferable. For occasional and other than continuous use, lead alloyed with about 6 per cent antimony is more satisfactory than pure lead.[67] It is sometimes necessary to remove from lead anodes an accumulation of lead chromate and peroxide.

It will be seen from the range of composition of the solution given in the last paragraph that the sulfate content bears a definite relation to the chromic acid content. That is, the ratio of CrO_3 molarity to SO_4 normality ranges from 100 to 50, although a ratio of 200 works satisfactorily. These proportions of sulfate have been found most suitable and are subjected to close analytical control. According to one theory the function of sulfate ions is to permit the formation of a soluble divalent chromium salt from which chromium can be plated. In the electrolysis of chromic acid, chromium is reduced from the hexavalent state to the trivalent and probably electrodeposited from the divalent ion.[68] In the absence of sulfate (or other anion of a soluble chromic salt) there is formed on the cathode in pure chromic acid upon electrolysis a colloidal basic compound of indefinite composition and low solubility known as "chromium chromate." Precipitation of this substance blocks further reduction and prevents the deposition of chromium. The character of electrodeposited chromium varies widely depending upon the nature of the basis metal, the temperature of the plating bath and the current density employed. Three types of deposit have been distinguished,[66] namely, "dull" or "frosty," "bright" and "milky." Dull deposits may be satisfactory if a bright appearance and smoothness of surface are not required, but for most applications the bright deposit with its mirror-like finish which requires no buffing is essential. The milky deposit is thin, relatively soft and inadequate for most purposes. In order to obtain the bright chromium deposit consistently, it is imperative that all plating conditions be carefully adjusted and controlled.

The optimum average current density for the production of a bright deposit from a bath of given composition operated at a given temperature depends upon the nature of the metal which is being chromium-plated. In Figure 42 [58] typical curves for the plating range of a chromic acid-sulfate bath upon steel, nickel, copper and brass are shown. It will be seen that the range of current densities at which a satisfactory bright deposit can be obtained is greater at high than at low temperatures. The advantage from a plating standpoint of copper as an undercoating is indicated and has been confirmed in later work by others.[69] It is claimed that bright chromium deposits may be obtained over a wider current density range from chromic acid solutions in which the fluoride ion is substituted for the sulfate ion.[70]

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[67] Baker, E. M., and Merkus, P. J., *Trans. Electrochem. Soc.*, 61, 327 (1932).

[68] There is a difference of opinion on the last point. See Kasper, C., *Bur. Standards J. Res.*, 14, 693 (1935); and also Liebreich, E., *Z. Elektrochem.*, 40, 73 (1934); Birükoff, N. D., Makariewa, S. P., and Timochen, A. A., *Korr. Metallschutz*, 11, 172, 193 (1935); Mueller, E., *Z. Electrochem.*, 40, 326, 344 (1934).

The throwing power of chromium plating baths is notoriously low, with the result that it is difficult to plate articles of irregular shape satisfactorily. Recessed areas are likely to receive little chromium and that which is deposited may be milky in appearance owing to the fact that the current densities in these areas fall outside the bright plating range illustrated in Figure 42. There seems to be little possibility of markedly improving the throwing power of the chromic acid plating bath by modifying its composition. The most favorable operating conditions for obtaining maximum throwing power are high temperature (55° C.) and high current density (35 amp./sq. dm.) coupled with low chromic acid and sulfate contents.[71]

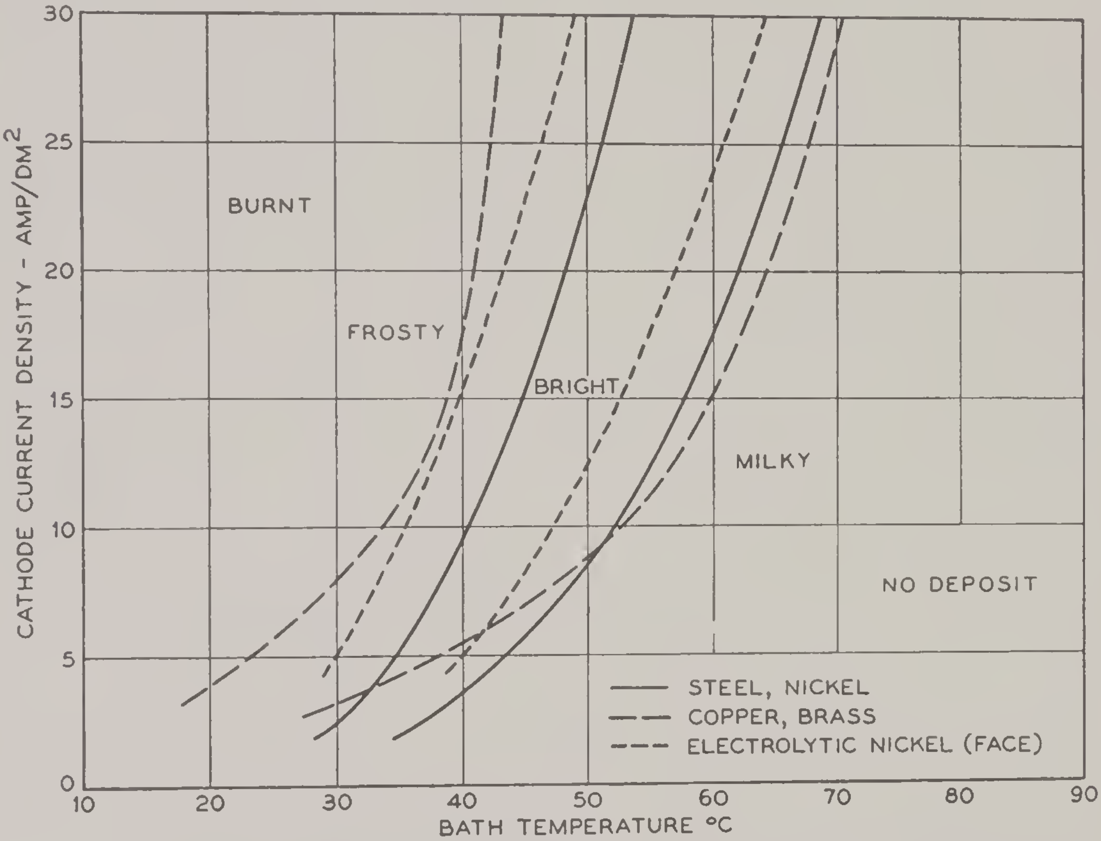

Figure 42.—The Effect of Basis Metal, Current Density and Temperature on the Character of Chromium Plating.

As would be expected a striking characteristic of chromium plating baths is their low cathode efficiency. This is rarely more than 20 per cent and is usually from 12 to 16 per cent for the production of bright deposits. The reduction of hexavalent chromium and the discharge of hydrogen gas accounts for the major portion of the current consumption.

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[69] Lukens, H. S., *Trans. Am. Electrochem. Soc.*, 53, 491 (1928); Cuthbertson, J. W., *Trans. Electrochem. Soc.*, 59, 401 (1931).

[70] Perlenfein, A., *Rensselaer Polytech. Inst. Eng. Sec. 5, Bull.* 39 (1933); also Curschmann, E., and Heinrich, H., *Monthly Rev. Am. Electroplaters' Soc.*, 23, 52 (Feb., 1936).

[71] Farber, H. L., and Blum, W., *Bur. Standards J. Res.*, 4, 27 (1930).

The hardness of chromium coatings expressed in Brinell units is 500 to 900,[72] a range of values which is higher than that reported for electrodeposits of any other metal. More recently values up to 1200 on the Brinell scale have been determined.[73] Platinum and rhodium deposits of Brinell hardness values of 640 [74] and nickel up to 550 [54] have been the nearest approach by other metallic coatings to the hardness of chromium.

The microstructure of chromium coatings, which is reflected in their high hardness, reveals crystals so fine that their detection is difficult under an ordinary microscope. By means of electrolytic etching in hot chromic acid containing a small proportion of sulfuric acid it has been found that the deposits generally contain numerous inclusions of foreign material. This investigation [73] has shown furthermore that both the composition of the plating solution and the conditions of electrolysis exert a distinct influence on the structure and hardness of chromium deposits. The effect of current density and bath temperature upon Brinell hardness is shown, for example, in Figure 43.

Chromium deposits upon copper and nickel are somewhat more uniform in character than those upon steel. Studies [75] have shown that in the deposition of chromium upon steel surfaces the deposit appears initially upon cementite areas and then spreads rapidly to the ferrite within the pearlite areas. Chromium may be plated directly upon aluminum [76] and upon zinc and zinc alloys,[77] but such coatings do not provide a very high order of protection to these materials.

The commonly used undercoating for chromium plate, as already mentioned, is nickel. Until the development of bright nickel it was necessary to buff the nickel deposit before application of chromium in order to obtain the required high luster of the chromium finish. This operation has been the most expensive step in the process, and its elimination is reducing the cost of the chromium finish appreciably.

A recent development of interest is the production of black deposits of chromium.[78] These coatings, which have a pleasing appearance, are deposited from solutions of chromic acid containing a small addition of acetic acid at current densities of 80-150 amperes per square decimeter (about 750-1400 amp./sq. ft.). The temperature of the bath is maintained below 15° C. (59° F.). Black chromium plate may be plated directly on steel, nickel or brass, but because of its higher cost it is generally deposited on a nickel-bright chromium coating.

[72] Becker, E., *Giesserei*, 18, 953 (1931).

[73] Cymboliste, M., *Trans. Electrochem. Soc.*, 73, 353 (1938).

[74] Atkinson, R. H., and Raper, A. R., *J. Electrodepositors' Soc.*, 9, 77 (1934).

[75] Ewing, D. T., Publow, H. E., and Tuttle, C. D., *Michigan State Coll. of Agri. Engg. Expt. Station Bull. No. 33* (1930).

[76] Work, H. K., and Slunder, C. J., *Trans. Electrochem. Soc.*, 59, 429 (1931); Altmannsberger, K., *Chem. Zeit.*, 55, 709 (1931).

[77] Anderson, E. A., and Reinhard, C. E., *Automotive Ind.*, 66, 528, 542 (1932); Thompson, M. deK., and Jelen, F. C., *Trans. Electrochem. Soc.*, 63, 141 (1933).

[78] Pollack, A., *Chem. Zeit.*, 59, 56 (1935); Weis, A., *Oberflachtentech.*, 13, 101 (1936).

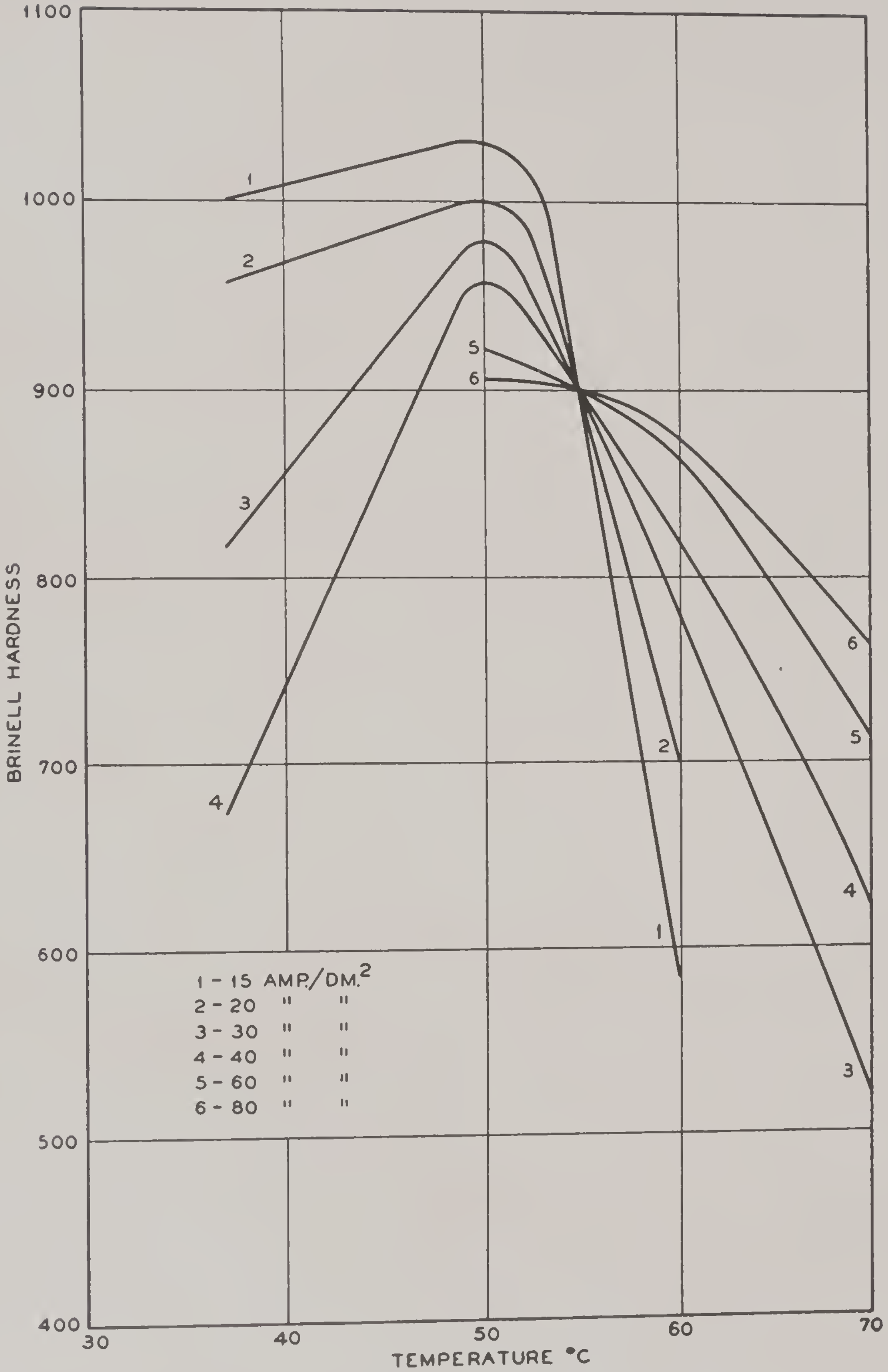

Figure 43.—The Effect of Current Density and Temperature of Bath Upon the Hardness of Chromium Plating.[73]

Chromium Cementation: "Chromizing"

A coating of chromium on iron may be produced by cementation in a manner analogous to that used for sherardizing. The parts to be treated are packed in a container with a mixture of 55 parts of chromium powder and 45 parts of alumina by weight and heated *in vacuo* or in an inert atmosphere, preferably hydrogen.[79] The material is usually heated to 1300-1400° C. (2370-2560° F.) for 3 or 4 hours in a molybdenum-wound furnace, although lower temperatures and shorter periods of heating may be used when less penetration is desired. Thus heating at about 1000° C. (1850° F.) for one hour will produce a casing about 0.004 to 0.005 inch in depth. The rate of penetration becomes accelerated above 1300° C., and when thicker coatings or higher concentrations of chromium are desired it is customary to operate in this temperature region. At a given temperature the depth of penetration is a linear function of time.[80] It is essential that oxygen and water vapor be excluded from the system, for otherwise at the high temperatures employed chromium is rendered inactive by the formation of a film of oxide which interferes with diffusion. Powdered ferrochromium has been used in place of chromium in chromizing.[81] While the process is usually carried out on finished or semi-finished steel articles another possible method of application is to produce a thick chromized coating on a bar or billet and then work these down to sheet, rod or strip stock.

The metals, chromium and iron, alloy very readily with one another. Although different investigators have reached varying conclusions concerning the equilibrium diagram of this alloy system, the fact that chromium readily goes into solid solution in iron is the essential and favorable condition for the chromizing process. The microstructure of a chromized iron sample is shown in Figure 44. The chromium is evidently in solid solution in the iron. The surface of a chromized metal is not exceptionally hard for it can be polished readily to a high luster. Iron or steel of low carbon content (0.10-0.20 per cent) can be chromized readily. High-carbon steels are difficult to treat unless their surfaces are previously decarburized by heating in hydrogen.[79] Ordinarily the chromium content of the diffused layer varies between 10 and 20 per cent. The behavior of a chromized metal upon heating is similar to that of a calorized material. The chromium diffuses deeper into the metal as the heating is continued and the chromium content of the surface layer is gradually reduced. For example, the chromium content of the surface layer on an iron sample which was treated for three hours at 1350° C. has been reported to be 10.4 per cent. By heating a similarly treated rod for three hours more in hydrogen the chromium content of the surface layer was reduced to 7 per cent.[79] The dimensions of iron or steel articles are not appreciably changed by the chromizing treatment.

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[79] Kelley, F. C., *Trans. Am. Electrochem. Soc.*, **43**, 351 (1923); U. S. Patent 1,365,499 (Jan. 11, 1921).

[80] Kelley, F. C., *Am. Soc. Metals Handbook*, 1938.

[81] Laissus, J., *Compt. rend.*, **180**, 2040 (1925).

The corrosion resistance of chromized steel is somewhat similar to that of high-chromium steels, although no very extensive studies appear to have been carried out. Chromized steel is resistant to steam and to atmospheric conditions. In the salt-spray test chromized iron resisted corrosion as well as sherardized specimens and after a month's exposure gave only slight evidence of attack. Specimens chromium-coated by this method were found to have a decided resistance to attack by dilute nitric acid, but were very readily attacked by dilute hydrochloric and sulfuric acids. It has been suggested that chromized nickel steel will withstand erosion exceptionally well when used in the construction of turbine buckets.[79]

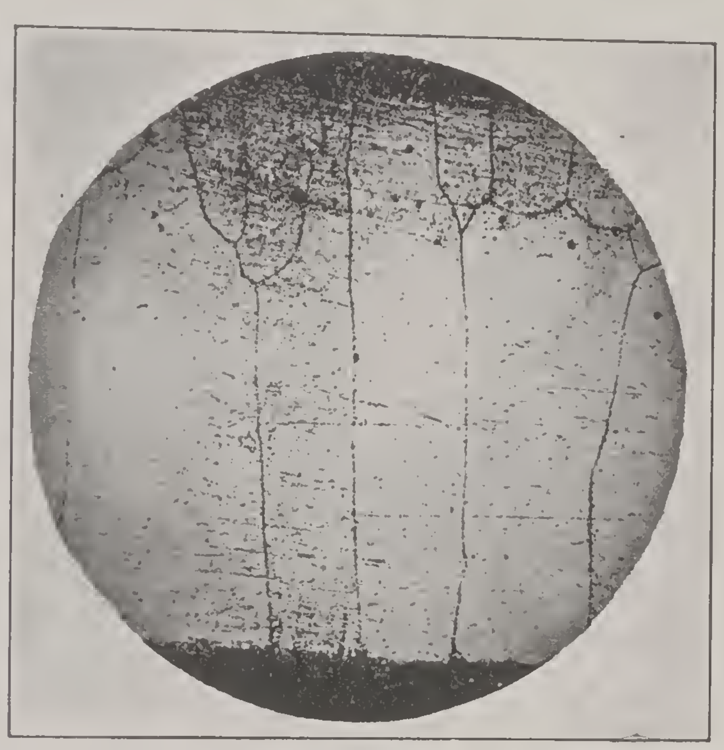

Figure 44.—Structure of a Coating Produced on Iron by "Chromizing," Heated for 4 Hours at 1350° C. ×50. The Upper Edge Corresponds to the Outer Surface of the Coated Material.[80]

Owing to the marked advances which have been made in chromium plating and in the development of a large variety of corrosion-resistant alloy steels, the chromizing process has not enjoyed the commercial use which otherwise would have been warranted by the quality of the product.

The Performance of Chromium-Plated Coatings

It is well known that a chromium surface upon exposure to air is immediately coated with an extremely thin and invisible oxide coating which protects the metal indefinitely from further attack. When physically injured this coating repairs itself. In the absence of oxygen and particularly if chlorides are present at the same time, the film on chromium is destroyed and the metal may suffer attack.

Electroplated chromium coatings in the thickness employed industrially are porous and often contain a network of fine cracks. By plating copper on chromium coatings it is possible to reveal the existence and the location of pores and cracks in the coating, the copper being deposited on these areas and not on chromium. The result of this experiment is shown in Figure 45.[82] Cracking is more likely to occur and to be more pronounced in thick coatings than in thin ones. A careful study[83] of the porosity of chromium coatings has shown that very thin coatings contain round pores which decrease in prevalence with increasing thickness of coat. Further increase in weight of coating is usually accompanied by the formation of cracks. There appears, therefore, to be an optimum thickness of coating (0.00002 to 0.00003 inch) which affords maximum protection. Changes in composition of the plating bath appear to have little effect on porosity,

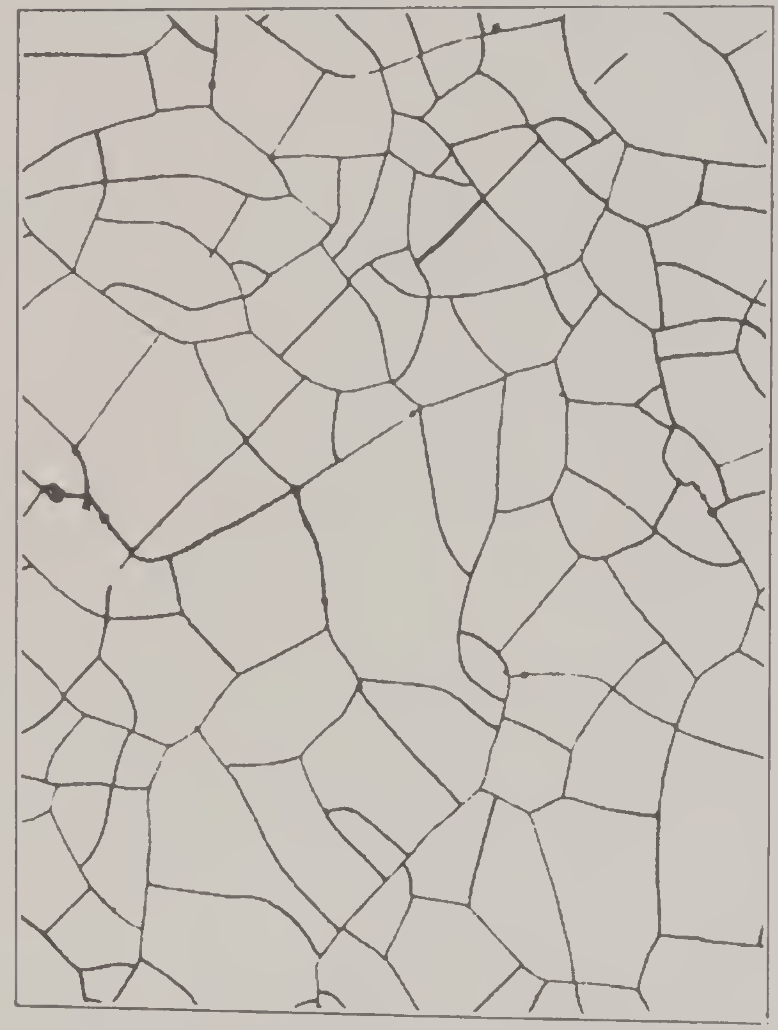

Figure 45.—Cracks (Lines) and Pinholes (Spots) in 0.00011-Inch Chromium Coating on Nickel Brought out by Copper Plating. ×100.[82]

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[82] Gillett, H. W., (Abstract of a lecture by W. Blum) *Metals and Alloys*, 2, 365 (1931).

[83] Blum, W., Barrows, W. P., and Brenner, A., *Bur. Standards J. Res.*, 7, 697 (1931).

while increasing the bath temperature from 45 to 65° C. was found to result in a marked decrease in porosity especially in thick coatings. It is the existence of pores and cracks in chromium deposits that accounts for their low protective value when used alone. When applied to brass exposed to corrosive conditions chromium coatings often become filmed with a brownish layer of corrosion products derived from the substrate. Applied directly to steel, chromium coatings develop pinhole rusting upon outdoor exposure. Consequently it has become the universal practice in the use of chromium plating to apply an undercoating, usually nickel, for protective purposes, and to employ a thin veneer of chromium on top of this for appearance.

Mention has previously been made in the section dealing with nickel coatings of the jointly-sponsored systematic atmospheric corrosion test on nickel coatings. Included in this test were specimens coated with chromium and composite coatings of nickel and of nickel-copper, cadmium and zinc with chromium as an outer layer.[50] The chromium coatings were deposited from the standard chromic acid-sulfate baths (with some variation both in concentration and in ratio of CrO_3 to SO_4). Nickel coatings upon which chromium was plated were previously buffed. The temperature of the chromium solution was varied from 35 to 65° C. (95 to 149° F.) and the current densities chosen to yield bright deposits at about 12 per cent cathode efficiency. In this connection it is of interest to note that the coatings produced at 35° C. were consistently about 15 per cent superior to those produced at the higher temperatures. Changes in the concentration of chromic acid did not affect the value of the coatings, but a decrease in sulfate content (*i.e.*, an increase in the ratio CrO_3 to SO_4) made a consistent improvement of about 20 per cent in coatings deposited at 45° C. and 16 amperes per sq. dm. The performance of the chromium finish exposed to various outdoor atmospheres in this exposure test is given in Table 24.

Table 24.—Protective Value of Various Composite Coatings with Outer Layer of Chromium.[50]

(Total thickness 0.001 inch including 0.00002 in. chromium)
18 months' exposure. Per cent scores.*

Set Number	Undercoat	Key West	New York	Pittsburgh	Sandy Hook	State College	Washington	Average (6)	Marine Average (K.W., S.H.)	Industrial Average (N.Y., P.)	Suburban Average (S.C., W.)
101	Ni 0.001	54	69	23	47	100	99	65	51	46	100
121	Zn 0.0005, Ni	81	47	20	65	85	80	63	73	34	83
123	Cd 0.0005, Ni	71	63	22	79	97	93	71	75	43	95
124	Zn 0.0002, Cu 0.0003, Ni	75	60	24	81	87	97	71	78	42	92
125	Cd 0.0002, Cu 0.0003, Ni	63	59	29	77	99	95	70	70	44	97
137	Cd 0.0005	38	67	64	78	93	87	71	58	66	90
138	Zn 0.0005	38	79	77	88	95	79	76	63	78	87

* For method of rating see Table 23.

The most striking feature of the results given in Table 24 is the excellent performance of all the coatings in the suburban atmospheres in contrast to the poor showing in the industrial regions. It is not surprising that the coatings gave evidence of failure in marine localities for it is general experience in the automobile field that the salt content of seaside atmospheres tends to cause rusting of nickel-chromium finishes. These findings are in agreement with the results for nickel coatings alone reported in Table 23 and indicate that the performance of the finish is determined largely by the behavior of the nickel component of the coating. Incidentally it has been estimated [50] that plated coatings which furnish satisfactory protection in such localities as State College and Washington for a year or more should last almost indefinitely under normal household or office conditions.

It is rather difficult to explain the variable results obtained in this investigation with intermediate zinc and cadmium coats. In general there appears to be no consistent advantage in composite coatings of this character and in many cases detrimental effects are obtained. Where chromium is applied directly over zinc or cadmium the finish develops a dull appearance after a few months' exposure, resembling the behavior of thin chromium coats on brass alluded to previously. Chromium coats 0.0002 inch in thickness applied to steel and exposed in the above test rusted badly within a few months and were generally inferior to specimens with 0.00025 inch of nickel or of copper and nickel.

Chapter 10

Coatings of Copper, Lead, Aluminum and Miscellaneous Metals

Copper Coatings

Copper is not ordinarily recommended as a coating for the protection of iron or steel against corrosion. An article completely coated with copper, if the coating were intact at all points, would, of course, resist corrosion as effectively as a piece of solid copper, but only so long as the coating remained intact. The cathodic behavior of copper with respect to iron when the two metals are in contact and wet with an electrolyte is more marked than the behavior of nickel in this respect. Copper, however, does not have the pleasing appearance of nickel and lacks the ability to retain a high polish, both of which are properties that favor the use of nickel as a coating metal in spite of its cathodic nature with respect to iron. As a general rule, copper coatings are used for other purposes than protection from atmospheric corrosion.

Coatings of copper may be deposited very readily by electroplating, by metal spraying and by mechanical coating processes. In addition, some special methods, as noted below, have been proposed.

Electroplated Copper Coatings

Firmly adherent coatings of copper can readily be deposited electrolytically. The two solutions in common use today, which have been used for a good many years, are the acid sulfate and the alkaline cyanide solutions. Recently a modification of the alkaline cyanide bath obtained by the addition of Rochelle salt (sodium potassium tartrate) has been shown to have desirable characteristics. Copper-plating by means of the acid-sulfate bath is limited somewhat, since this solution cannot be used for plating directly upon iron. The "spongy" copper deposited on the surface of the iron upon immersion in copper sulfate solution prevents subsequent deposition of an adherent coat. For coating iron or steel, therefore, the cyanide solution must be used, at least at the start, although it has been stated[1] that copper can be plated directly upon iron provided the iron has been covered with a film of arsenic by being dipped into a solution of arsenic trioxide in concentrated hydrochloric acid. The alkaline cyanide plating bath, however, is generally a much more convenient means of copper-coating iron and steel than is such a solution of arsenic. A copper plating bath containing a complex sodium-copper oxalate salt known as disodium diaquo-dioxalatocupriate has been proposed as suitable for plating copper directly on steel.[2] Copper may be deposited from solutions of a variety of other copper salts, for example, from alkaline copper iodide solutions, forming in this case deposits which under some conditions contain iodine (or iodide).[3] Baths of this type, however, are of no commercial importance.

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[1] Watts, O. P., *Trans. Am. Electrochem. Soc.*, 35, 265 (1919).

The acid-copper bath consists essentially in a solution of copper sulfate containing sulfuric acid, the proportion of the two constituents varying over fairly wide limits. For example, 150 to 240 grams per liter of $CuSO_4 \cdot 5H_2O$ (20-32 oz./gal.) and 50 to 75 grams of sulfuric acid per liter (6.7 to 10 oz./gal.) is a suitable concentration range for the production of satisfactory coatings under the ordinary conditions of operation.[4] Current densities up to 10 amperes per square decimeter (93 amp./sq. ft.) may be employed at ordinary temperatures, while at 45° C. (113° F.) double this current density is practical. Usually, however, somewhat lower current densities are used in copper plating. Addition agents, such as glue and more particularly phenol-sulfonic acid, have been recommended[5] for use in the acid bath when thick, smooth, fine-grained deposits are desired. Phenol up to 10 grams per liter may be used to produce smooth, hard and ductile coatings.[6] The cathode efficiency of the acid-sulfate-copper bath is generally in the neighborhood of 100 per cent. Copper anodes of high purity are readily available in either the electrolytic, cast or rolled forms, the latter being usually the most satisfactory.

The alkaline copper cyanide solution consists principally of the complex salt $Na_2Cu(CN)_3$ with varying amounts of carbonate and hydroxide. A typical commercial formula[4] for this bath contains 22.5 grams per liter of cuprous cyanide (3 oz./gal.), 34 grams per liter of sodium cyanide (4.5 oz./gal.) and 15 grams per liter of sodium carbonate (2 oz./gal.). The bath is usually operated from 30-40° C. (86-104° F.) and at current densities from 0.3 to 1.5 amperes per square decimeter (2.8-14 amp./sq. ft.). The cathode efficiency is from 50-90 per cent. Owing to the small dissociation of the complex copper cyanide ion $[Cu(CN)_3]^-$ the concentration of cuprous ions in the bath is very low. For this reason the alkaline cyanide bath possesses good throwing power. Deposits obtained from the bath are fine-grained.

The use of Rochelle salt in alkaline copper cyanide solutions permits the use of appreciably higher current densities.[7] The optimum composition for this bath is:

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[2] Fink, C. G., and Wong, C. Y., *Trans. Electrochem. Soc.*, 63, 65 (1933).

[3] Schlötter, M., Korpiun, J., and Burmeister, W., *Z. Metallkunde*, 25, 107 (May, 1933); see also Schlötter, M., *Trans. Faraday Soc.*, 31, 1177 (1935).

[4] Blum, W., and Hogaboom, G. B., "Principles of Electroplating and Electroforming," 2nd ed., New York, McGraw-Hill Book Company, 1930.

[5] Ollard, E. A., and Perring, J. W., *Met. Ind. (London)*, 45, 277, 423, 519 (1934).

[6] Hull, R. O., and Blum, W., *Bur. Standards J. Research*, 5, 767 (1930); Hothersall, A. W., *Electroplaters and Depositors Tech. Soc. Preprint*, March, 1931.

[7] Graham, A. K., and Read, H. J., *Metal Ind. (N. Y.)*, 35, 559, 617 (1937); 36, 15, 77, 120 (1938).

Substance	Ounces/gallon	Grams/liter
Cuprous cyanide	3.5-5.5	26.2-41.2
Sodium cyanide	4.6-6.8	34.5-51
Free cyanide	0.75	5.6
Rochelle salt	8.0	60.
Sodium carbonate	4.0	30.

The pH of this mixture is 12.7.

The bath is operated in the temperature range 140-190° F. (60-88° C.) at cathode current densities from 20-90 amperes per square foot (2.16-9.7 amp./sq. dm.). When lustrous deposits are desired, as in plating die-castings prior to coating with nickel and chromium, the bath concentration is maintained at the lower values which are proposed.

Structure of Electroplated Copper Coatings

The microstructure of electrodeposited copper may be described in some detail since it is typical of many features common to electroplated coatings. For example, electrodeposits of copper usually consist in columnar or finger-like crystals arranged perpendicularly to the surface of deposition, that is, parallel to the direction of current flow. This is shown in Figures 46 and 47. The grain size and hence the hardness and strength of the deposited coating depends upon several different variables of deposition. For instance, an increase in current density results in a smaller grain size as well as a more irregular structure, a condition usually accompanying higher strength and hardness. Copper deposits made by use of cyanide solutions have a very fine grain size. Likewise addition agents, usually of a colloidal nature, in a plating bath aid in producing a very small grain size. Some of the colloidal matter is carried to the cathode where it obstructs the grain-growth of the deposit in which it is incorporated. The fine fibrous structure produced by the presence of colloids has been shown to be much harder than the large columnar crystalline deposit obtained in the simple acid sulfate bath.[8]

Addition of lead in amounts of 0.1 to 0.01 gram per liter to alkaline copper cyanide baths improves the brightness of the deposit markedly, the structure of the deposit being dense, compact and slightly banded.[9] Fractional percentages of lead are codeposited with copper in this instance. The banded structure appears to be associated with a fluctuation in deposition potential resulting in periodic deposition of the metal. Evidence has been educed [10] to show that "brightness" of deposits is related to the perfection of the orientation of the crystallites of the deposited metal. Very possibly the brightness of copper deposits induced by small amounts of lead may be the result of an alternate deposition of foreign matter (basic salts or lead) and oriented copper.[9]

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[8] Macnaughton, D. J., and Hothersall, A. W., *Trans. Faraday Soc.*, 31, 1168 (1935).

[9] Meyer, W. R., and Phillips, A., *Trans. Electrochem. Soc.*, 73, 377 (1938).

[10] Schlötter, M., *Korr. Metallschutz*, 5, 16 (1929); Wood, W. A., *Trans. Faraday Soc.*, 31, 1248 (1935).

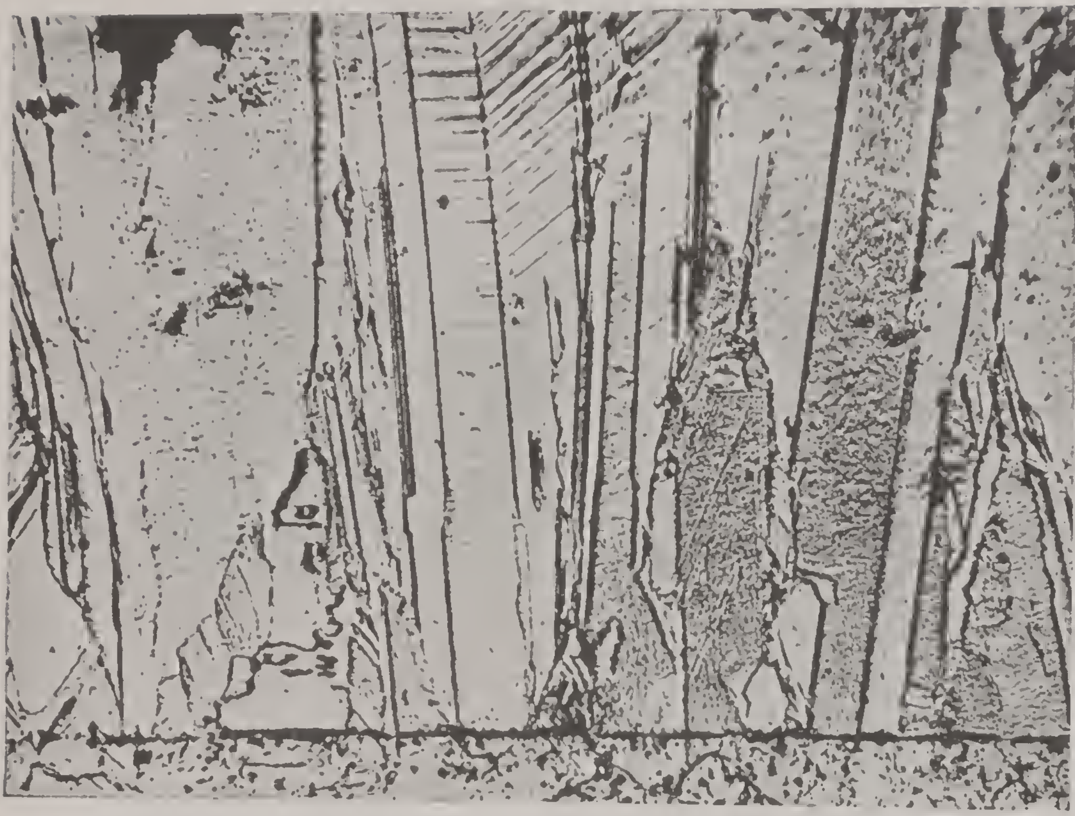

Figure 46.—Columnar Crystal Structure of Deposit Perpendicular to Surface of Deposition.[9]

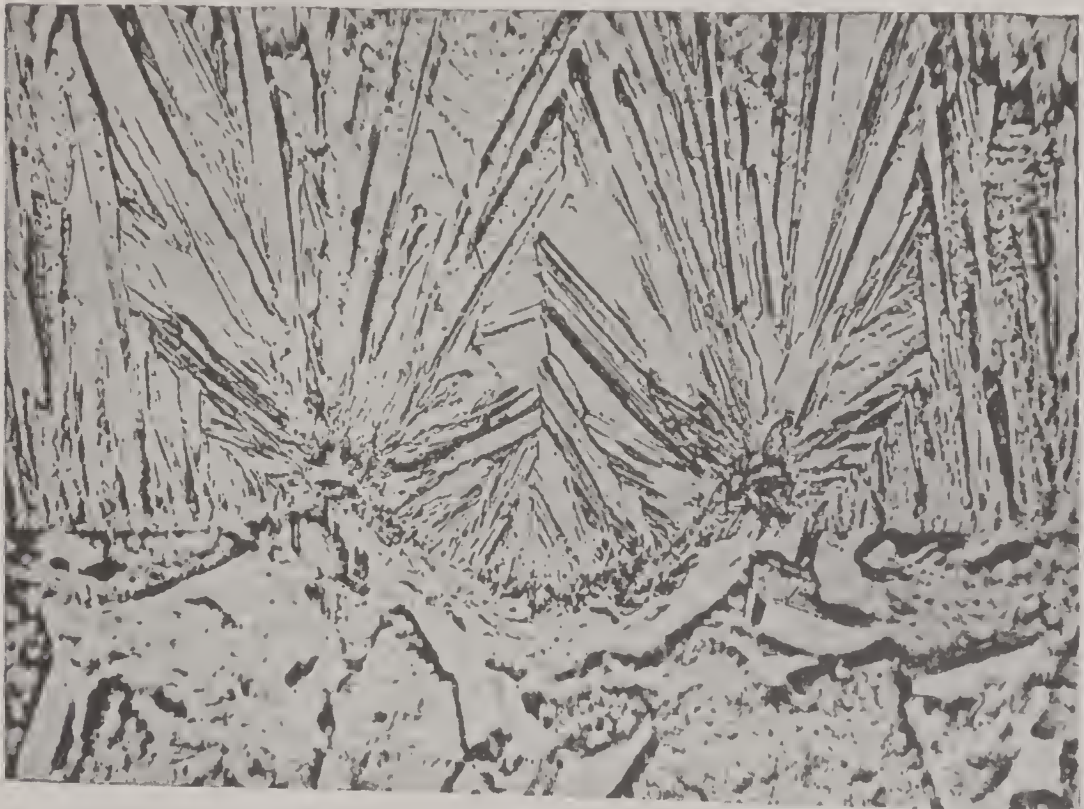

Figure 47.—Orientation of Crystals Deposited upon a Scratch in Basis Metal. Acid Copper Solution. Current Density 1 amp. per. sq. dm.[9]

Upon annealing electrodeposited copper there is usually a complete recrystallization of the metal. It would appear that the copper layer as deposit is not in a state of structural equilibrium but rather in a condition somewhat akin to cold-worked metal. This condition of electrodeposited metals with respect to internal stresses is probably of some significance in accounting for the hardness of such materials.[11]

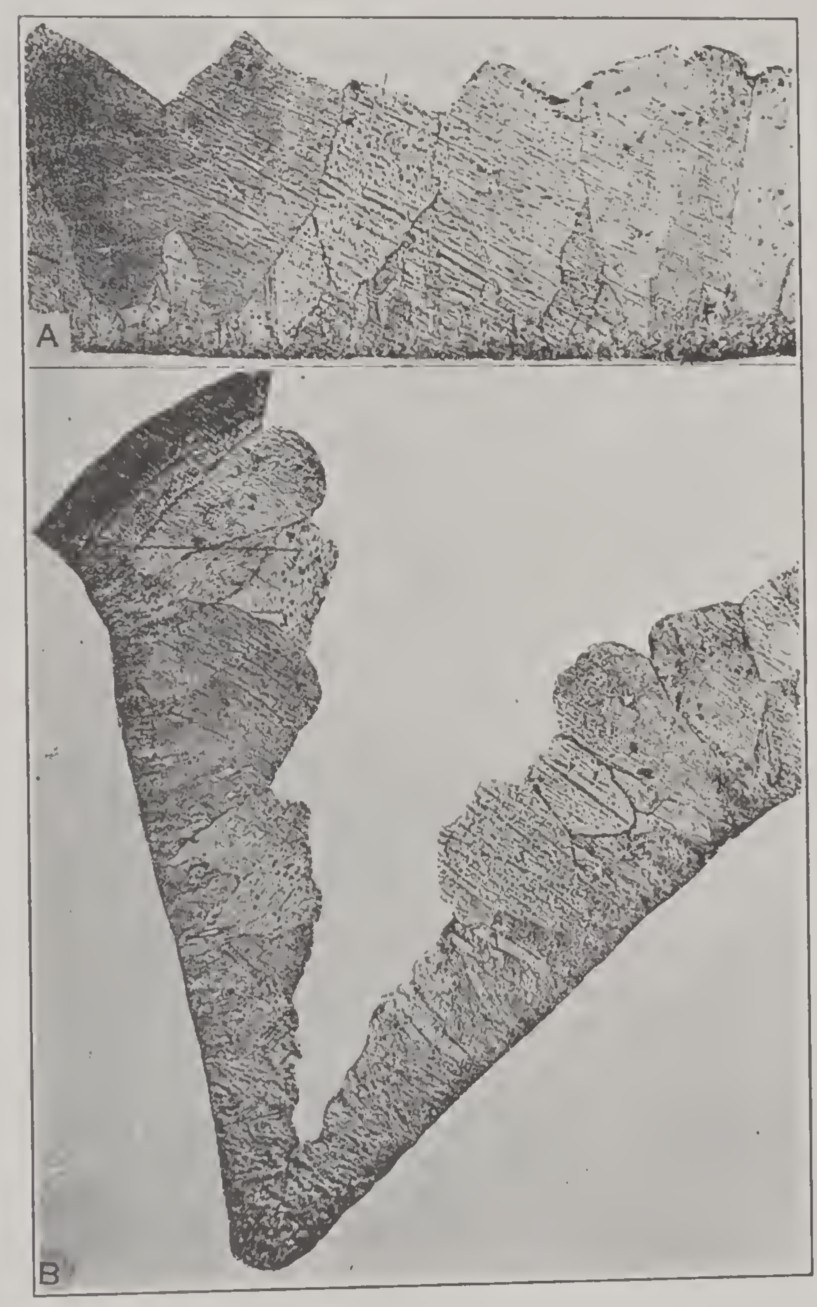

Figure. 48.—Variation in Coating Thickness of Electrodeposited Copper Depending on Contour of Surface. ×150. [Blum, W., Holler, H. D., and Rawdon, H. S., *Trans. Am. Electrochem. Soc.*, 30, 159 (1916)].

The uniformity in thickness of an electroplated coating depends largely upon the shape of the article plated. As is shown in Figure 48 the thickness of a copper coating at the base of a depression such as a V-groove may be not more than one-quarter the average thickness of the coat.

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[11] Macnaughton, D. J., *J. Iron Steel Inst.*, 109, 409 (1924).

Adhesion of Electroplated Copper Coatings

The adherence of electroplated coatings is a matter of great practical importance. Unlike coatings produced by hot-dipping there is usually little if any diffusion of electroplated coatings into the basis metal. It is obvious, of course, that the surface to be plated must be clean if good adherence is to be obtained; the presence of oxides, sulfides, and extraneous materials such as grease may reduce adherence to the point where the coating peels from the surface. As has been pointed out in Chapter 2, deposits adhere more firmly to roughened surfaces because of the greater opportunity of physical anchorage which is thereby provided. That the removal of the disturbed or "disorganized" surface layer of a metal is often conducive to a higher degree of adherence is evident from experiments[12] in which copper was deposited on copper surfaces which had been etched with acid following the ordinary chemical cleaning. In this case it was found that the crystals in the plated layer were simply extensions of the surface crystals of the base, that is, it would appear that the strength of the bond between coating and base metal must approach in magnitude that existing between atoms in a solid. When, however, the base metal was merely cleaned without being etched, the deposited layer was firmly adherent, but without any evidence in its structure of having been influenced by the structure of the base metal. It is of interest to note that in the case of copper which had been cold-rolled so that the crystalline structure throughout the sheet was considerably disturbed and broken, the structure of the deposited layer on an acid-cleaned specimen showed only very slight evidence of any tendency to "repeat" the structure of the base.

Presumably the continuation of the microstructure of the basis metal in the electrodeposit is favored by relatively large crystals in the basis metal and conditions of plating which are conducive to the deposition of crystals of similar size. Interference with crystal growth by the inclusion of foreign ions, atoms or molecules tends to produce fine-grained deposits incapable of following the pre-existing crystal structure of the substrate. Recent studies[13] have shown that electrodeposited copper (and to some extent nickel and tin) may continue the microstructure of other metals when the deposit and basis metal belong to the same crystal system over a range of differences in lattice parameters, and even in some cases when deposit and basis metal belong to different crystal systems. In Figure 49 are shown examples of the continuation in electrodeposited copper of the crystal structures of certain specimens of rolled copper, nickel and silver.

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[12] Blum, W., and Rawdon, H. S., *Trans. Am. Electrochem. Soc.*, 44, 305 (1923).

[13] Hothersall, A. W., *Trans. Faraday Soc.*, 31, 1242 (1935).

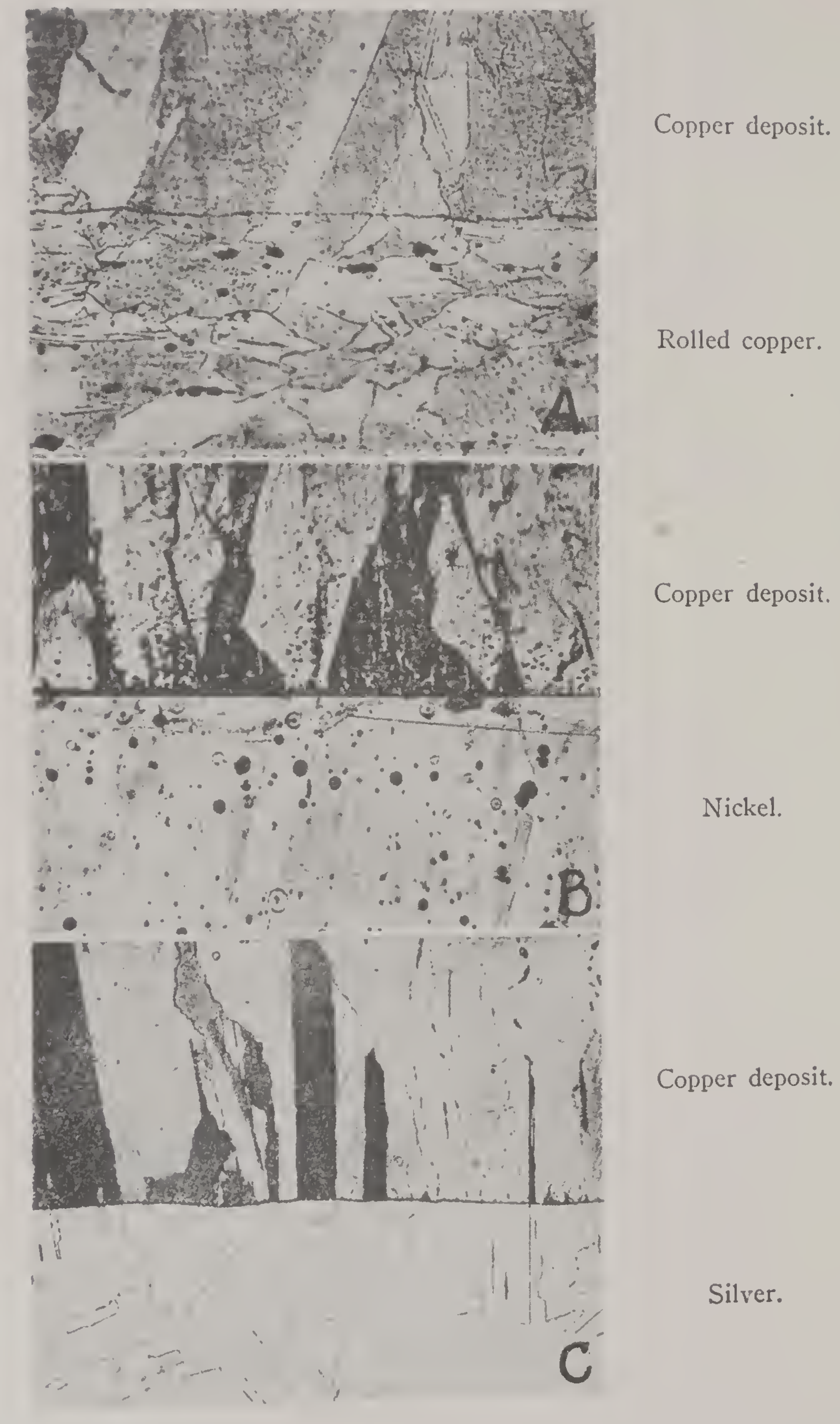

Figure 49.—Continuation of Structure of Basis Metal in Electrodeposited Copper.[18]

A. On Rolled Copper (× 133).
B. On Annealed Nickel (× 66).
C. On Annealed Silver (× 133).

Use of Electroplated Copper in Selective Carburization of Steel

It is often necessary in the case-hardening of steel parts that portions be left in their initial or relatively soft condition to allow machining to be done in such parts or to enable the piece to be straightened after hardening. Copper coatings play an important part in this process. Those portions of the surface which are to remain soft are electroplated with copper before the steel parts are packed in the carburizing mixture. This may be accomplished either by plating the entire surface with copper, usually in an alkaline cyanide bath, and then removing it mechanically from the areas to be hardened; or by coating the areas to be hardened with a baked japan or "stopping-off" compound, and then plating the bare surfaces to be protected, the organic finish being later burned off in the carburizing operation. At the close of the carburizing treatment, it is found that the presence of the copper layer has prevented carburization of the underlying steel and hence such parts do not harden appreciably when the piece is heated and quenched.

Copper applied by the metal-spraying process has been found to be effective in protecting against carburization.[14] Such a layer must be somewhat thicker than one which is electroplated, since the metal-sprayed layer may be slightly porous. The process is to be recommended because of the ease with which it can be used in applying a copper layer to a few spots, here and there, on an article to be carburized. It is a very simple matter to localize the deposit. Other conditions have favored the use of electroplating, however, and the metal-spraying process has not, as yet, found application in commercial carburizing plants in this country.

It is generally agreed that any coating that will prevent the access of the carburizing gas (carbon monoxide) to the underlying steel will answer the purpose.[15] Copper is the most useful of the metals, however. Nickel coatings, for example, are not suitable for the purpose as the carbon monoxide readily permeates them and carburizes the steel beneath. Cobalt would be expected to behave similarly and the melting points of the other coating metals commercially available are so much lower than the temperature used in carburizing as to be of no value. In practice, various kinds of non-metallic cements and pastes, sometimes containing powdered metals, are used.[16] They are not so dependable, however, as copper plating.

A layer of copper 0.005 inch thick is generally considered sufficient for practically any purpose. Studies have shown[17] that thinner coatings, for example, 0.0005 inch, will prevent carburization for periods up to 12 hours (at 1700° F.) and markedly retard penetration of carbon into the protected area for longer periods of treatment.

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[14] Guillet, L., and Bernard, V., *Rev. Métal*, 11, 752 (1914); *Iron Age*, **95**, 304 (1915).
[15] McCullough, J. C., and Reiff, O. M., *Ind. Eng. Chem.*, **16**, 611 (1924).
[16] Galibourg, J., and Ballay, M., *Rev. Métal*, **19**, 222 (1922).
[17] Vanick, J. S., and Herschman, H. K., *Trans. Am. Soc. Steel Treat.*, **4**, 305 (1923).

Mechanical Copper-Coating Process

The coating of steel with copper by use of the molten metal has been the subject of active investigation since the early part of the last century.[18] The difficulties attendant upon the high temperature necessary in using molten copper have precluded the use of the simple hot-dipping process.

The two metals alloy quite readily although they are not completely miscible in the molten state. Copper, at a temperature just below its melting point (1083° C., 1981.4° F.), can hold in solid solution approximately 3 per cent of iron. At the same temperature, iron dissolves approximately 8 per cent of copper. In both cases, the limit of solid solubility of one metal in the other decreases, as the temperature is lowered, to considerably less than one per cent at room temperature. Most alloys of the two metals therefore will consist of two constituents which are the two solid solutions, the relative amount of each constituent depending upon the composition.

In brief, the mechanical method which has been developed for coating steel with copper is to prepare a composite or duplex billet or ingot having a steel center and a copper casing, which is then rolled or drawn down to the desired shape. No unusual difficulties have been experienced in rolling such a composite billet, and the copper coating which results is much more impervious than an electrodeposited one of the same thickness.

Different methods have been proposed for the preparation of the duplex billet. According to one method described for "copper clad" steel,[19] the properly cleaned steel billet is heated red-hot and then momentarily immersed in a hot bath of molten copper to form a very thin uniform alloy layer over the entire surface, after which molten copper at a much lower temperature is cast around the billet. The casting is accomplished by means of a special mold, which, with the billet inside, is immersed in the bath of molten copper.

In order to minimize the formation of an alloy layer between the two metals, the "copper-weld" process was developed. This method consisted in electroplating the cylindrical steel billet with copper and then enclosing it in a neatly fitting cast-copper tube.[18] After luting the crevices at the end to prevent access of air, the billet was heated to approximately 950° C. (1740° F.) and then worked into the desired shape. An earlier and somewhat similar process [20] consisted in dipping the steel billet in molten copper to form a thin layer over the surface and then adjusting the copper sleeve and working it into shape as just described.

The method of casting copper directly around a hot steel billet enclosed in a suitable mold [21] is the simplest and is used commercially today. The composite billet can readily be worked mechanically at a temperature of 900° C. (1650° F.). The properties of the finished coated product do not appear to be adversely affected by any increased alloying of the copper and iron which may result from this method. Brass and cupronickel may also be used for coating steel by this method.

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[18] Handy, J. O., *J. Ind. Eng. Chem.*, **5**, 884 (1913).

[19] Tassin, W., *Proc. Am. Soc. Testing Materials*, **10**, 280 (1910).

[20] Eldred, B. E., *Am. Machinist*, **30**, 474 (1907).

[21] Silverman, A., *Discussion, Trans. Am. Inst. Mining Met. Eng.*, **60**, 370 (1919).

Most of the steel coated with copper in this way is made into wire. The combination of high electrical conductivity and high tensile properties make this material a very useful one. The amount of copper used is dependent upon the desired conductivity of the finished wire. Such wire is usually designated in terms of the conductivity of a copper wire of the same size, for example, "30 per cent and 40 per cent conductivity." It is possible to obtain a minimum copper thickness at any point around the wire of 10 per cent of the wire radius on the 30-per cent grade and 12.5 per cent on the 40-per cent grade.[22]

Some use has also been made of copper-coated wire in screen cloth. Some copper-coated sheets rolled from a composite bloom have been made and used to a very limited extent for spouting, eaves-troughs and the like. Its use for bullet jackets has given very encouraging results. During the war, instead of the usual cupronickel bullet jacket, the Germans developed one made from a soft steel sheet coated with cupronickel by a process similar to that described above.

Miscellaneous Copper-Coating Methods

Richards[23] has described a method for coating steel with copper in which the copper is reduced from the oxide and melted *in situ,* that is, on the surface to be coated. The reduction of copper oxide by reducing gases, such as carbon monoxide or hydrogen, begins at a relatively low temperature, for example, as low as 130° C.[24] A mixture of powdered copper and copper oxide in crude oil ground to the consistency of a light varnish was applied to sheet steel while cold by means of rolls much like the inking rolls on a printing press, and the coated sheets were then conveyed by a chain conveyor into a furnace maintained at a temperature well above the melting point of copper. It was claimed that the oil base reduced the copper oxide present and also prevented oxidation of the copper which melted on the surface of the sheet. Although the method has been tried on a commercial scale, apparently with pronounced success, such sheets are not regular commercial materials.

The process is an adaptation of the earlier Siemens process used for the "coppering" of carbon brushes for electric generators and motors. In the Siemens process, the copper film is formed on the surface of the carbon by packing the brushes in finely divided copper mill scale (oxide) and heating to a temperature of approximately 400° C. The reduction of the oxide to metallic form gives a very adherent thin film of copper on the surface of the carbon. A process carried out in a manner quite similar to the Richards process is also utilized in ceramic work.

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[22] Whitney, L. C., "Am. Soc. Metals Handbook," 1938.

[23] Richards, J. W., *Trans. Am. Inst. Mining Met. Eng.*, **60**, 365 (1919).

[24] Palmer, W G., *Trans. Am. Electrochem. Soc.*, **51**, 445 (1927).

A method often employed for producing a copper finish on wire consists in immersion of the wire in a solution of copper sulfate. The precipitated spongy copper is rendered firmly adherent by drawing the wire through a die and reducing it in size very slightly. The coating thus formed is primarily for improving the appearance of the wire rather than for protecting it from corrosion. Finally, copper coatings are readily produced by metal spraying, sputtering and evaporation methods.

Corrosion Resistance of Copper Coatings

As previously stated in this chapter the successful use of copper coatings for the protection of iron or steel is largely dependent upon the absence of pinholes or defects in the coating which expose the underlying metal. Electroplated copper coatings in the range ordinarily deposited are porous. This does not impair the usefulness of such deposits as undercoatings for nickel and nickel-chromium finishes and they are extensively used for such purposes. Sputtered coatings may be obtained which are non-porous; and, of course, mechanically applied copper coatings (*i.e.*, "copper clad" or "copper-welded") also fall in this category.

Electroplated copper coatings were formerly employed to a limited extent on apparatus parts used indoors and in protected locations where the appearance of the article was of no importance. In air at low relative humidities, copper readily tarnishes, the weight gain with time showing a parabolic relationship. At higher humidities pinhole rusting occurs on electroplated coatings on steel. In the case of pore-free coatings the unattractive tarnish film in outdoor exposures is succeeded in time by the development of the green patina characteristic of copper in such atmospheres. Studies[25] of this coating have shown that its main constituent is usually basic copper sulfate, $CuSO_4 \cdot 3Cu(OH)_2$, although near the sea it may contain varying amounts of basic chloride. Basic copper carbonate is present always in minor proportions. It has been claimed[26] that the protective agent in the patina is cuprous oxide under all circumstances. A synthetic patina may be produced on copper by anodic oxidation in a suitable electrolyte.[27]

Steel clad with copper by the mechanical process is employed for ground rods and anchor rods, in which case direct contact with soils is involved. Limited tests[28] made on rods of this type buried in three soils have shown results similar to those obtained for copper. In an acid muck (where the oxygen concentration is low) the copper-coated rods were but slightly attacked. This is in accordance with general experience with copper in acidic environments in the absence of oxygen. For example, recent studies[29] have shown that the rate of corrosion of copper in sulfuric acid is directly proportional to the solubility of oxygen up to a concentration of $25N$, beyond which the oxidizing character of the acid influences the rate. Incidentally, the presence of nitrates or other oxidants in the soil is known to cause marked corrosion of copper. In an arid, highly alkaline soil the rate of corrosion of the copper coatings was less than half that of bare ferrous specimens in the same soil. The attack was, however, characterized by pitting, which after four years extended through the coating in one instance. The most severely corrosive soil for the copper-clad specimens (although the coatings were still intact) was a salt marsh on the New Jersey coast. Similar results were obtained for copper pipe in the soil burial test conducted by the National Bureau of Standards.[30] Copper pipes buried at this location showed an average loss of weight of 0.57 ounce per square foot per year in this soil as contrasted with an average of 0.067 ounce per square foot per year in the other 33 soils employed in this test. The corrosiveness of tidal marshes toward copper is not due to sodium chloride but to sulfides apparently resulting from the bacterial reduction (by *Spirillum desulfricans*) of sulfates.[31] The corrosion product is copper sulfide which, upon attaining an appreciable thickness, may be scaled off in slabs. The odor of hydrogen sulfide is readily detected upon spading up the soil at this location and in other similar marshes.

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[25] Vernon, W. H. J., and Whitby, L., *J. Inst. Met.*, 42, 181 (1929); 44, 389 (1930). Also, Freeman, J. R., and Kirby, P. H., *Metals and Alloys*, 3, 190 (1932); Vernon, W. H. J., *J. Chem. Soc.*, p. 1853 (1934).

[26] Haase, L. W., *Z. Metallkunde*, 26, 185 (1934).

[27] Vernon, W. H. J., *J. Inst. Metals*, 49, 153 (1932).

[28] Unpublished results reported by R. M. Burns and C. L. Hippensteel to the National Bureau of Standards Corrosion Conference in Washington, D. C., 1930.

Lead Coatings

Lead has many desirable features as a coating metal. Lead-coated sheet may be very seriously deformed without having the coating stripped off; hence such material finds considerable application in deep-stamping operations in which the coating aids materially by acting as a lubricant. The paint-holding properties of lead coatings are excellent. Lead is the only common coating metal which is resistant to sulfuric and sulfurous acid fumes.

Coatings of lead or lead-rich alloys are deposited by the hot-dipping process, by electroplating, and by the metal-spray process. Of greater importance, particularly in the chemical industry, are what is known as homogeneous lead linings which are applied to a great variety of equipment such as storage tanks, drums, autoclaves, pipes, agitators, propellers and mixing devices of all descriptions.[32] These coatings usually have a minimum thickness of $\frac{3}{16}$ inch.

The Hot-Dipping Process

When an iron or steel article is immersed in a bath of molten lead, no alloying occurs between the two metals even though the surface may have been thoroughly cleaned before immersion. The molten lead, therefore, does not readily "wet" the surface as zinc and tin do, and instead of forming a thin surface film over the immersed article, the lead coalesces more or less into drops and rivulets when the article is withdrawn from the lead bath. The same is true of brass and copper articles immersed in molten lead. Although lead coatings can be produced on iron and steel if great care is taken in cleaning the surface before attempting the hot-dipping process, such coated articles are always more or less unsatisfactory on account of the pronounced discontinuities that exist in the coating. The claim has been made [33] that if clean steel is dipped in a fluxing bath, consisting of a saturated solution of zinc chloride containing 5 per cent ammonium chloride, immediately before immersion in the molten lead (at 340 to 360° C.), a quite uniform coating of lead can be produced. Usually it is necessary to give the article two dips both in the flux and the lead bath.

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[29] Damon, G. H., and Cross, R. C., *Ind. Eng. Chem.*, 28, 231 (1936).

[30] Logan, K. H., *Bur. Standards J. Res.*, 7, 585 (1931).

[31] von Wolzogen Kühr, C. A. H., *Water en Gas*, 26, 277 (1923); von Wolzogen Kühr, C. A. H., and van der Vlugt, *Water*, 16, 147 (1934); Bunker, H. J., *Corrosion Committee of Iron and Steel Inst. Fifth Report*, Sec. F(3), page 431 (1938).

[32] Mantius, E., and Freiherr, H. F., *Ind. Eng. Chem.*, 29, 373 (1937).

In order to form a "bond" for a lead coating, it has been the practice in the past to make use of some alloying element common to the two metals, lead and iron. Tin has been used for this purpose for many years as it alloys readily with both metals. Antimony may be used [34] and cadmium [35] and mercury [36] have also been tried with some success. Arsenic has also been recommended.[33]

The alloying element may be added in a considerable amount to the lead bath as is the case in the manufacture of terne-plate described below; or a film of the alloying element may be precipitated on the surface of the article to be coated by immersion in a suitable solution prior to passing through the molten metal bath. Electroplating with a suitable bonding metal before dipping in order to form the desired bonding film has also been used to a limited extent.

Lead coatings show a rather pronounced tendency toward formation of pinhole perforations as the coating solidifies. In the case of sheets such perforations can be removed by rolling the sheet after it has been coated. On articles of irregular shape, however, this cannot be done.

A process has been described [34] for the production of coatings of relatively pure lead on iron and steel. The material, after pickling, is immersed in a solution of antimony chloride; the film of precipitated antimony, by its alloying action after immersion in the bath of molten metal, serves as a binder for the coating. The molten metal bath used may be either commercially pure lead or an alloy of lead and antimony.

Antimony alloys very readily with lead. The two form a simple eutectiferous series, the eutectic containing 13 per cent antimony and melting at 247° C. The limit of solubility of antimony in solid lead has been shown [37] to be as low as 0.5 per cent at room temperatures increasing to 2.45 per cent at the eutectic temperature. Antimony also alloys readily with iron forming two compounds, Fe_3Sb_2 and Fe_2Sb_2, which have been reported in this alloy system.

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[33] Maass, E., *Korr. Metallschutz*, 1, 76 (1925), *Met. Ind. (London)*, 27, 557 (1925). Also Westerkamp, H., *Chem. Ztg.*, 49, 1056 (1925).

[34] Baskerville, Chas., *J. Ind. Eng. Chem.*, 12, 152 (1920); U. S. Patent 1,378,439 (1921).

[35] Beneker, J. C., *Am. Gas Light J.*, 103, 292 (1915); U. S. Patent 1,144,523, (June 29, 1915).

[36] *Iron Age*, 89, 644 (1912); *Met. Chem. Eng.*, 10, 253 (1912). Also, *Iron Age*, 99, 1483 (1917).

A somewhat similar process, in which the articles to be coated were passed through a solution of mercuric chloride, has been tried on a commercial scale. The film of precipitated mercury served as the basis of the alloy-binding layer. On account of the dangers attending the use of the poisonous mercury solution, however, the process did not prove a commercial success.[36]

Some excellent "lead-coated" sheets have been made by using galvanized stock as a base upon which the lead coating was formed by immersion in molten lead. Commercial tin plate can be used in the same way as a base for subsequently coating with lead. A recent investigation [39] of lead-dipped coatings applied over zinc-plated steel has shown that a smooth, adherent, continuous coating of lead may be obtained within narrow limits of bath temperature, provided the molten lead contains a fractional percentage of zinc. The binding agent in this case appears to be needle-like crystals of zinc which extend into the lead layer and attach themselves through a solid solution of zinc in lead.

Lead Linings

A substantial veneer of lead on iron or steel, producing a duplex metal structure, is known as a lead lining, and is to be distinguished from the thinner coatings or coverings of lead obtained by hot dipping or electroplating. For many years, more or less loose linings of lead sheet have been used in supporting vessels of wood, brick or steel. In other instances such linings or coverings have been fastened or bonded at certain points.

In the early development of homogeneous lead linings, tin or solder was used to bond the lead layer to the steel. In recent years it has been possible to attain this end by the use of non-metallic fluxes, usually of secret nature. The steel surface is first cleaned thoroughly and pickled or sandblasted, before application of the flux. There are two general methods of application of the lead layer; molten lead may be poured on the fluxed surface or it may be "burned" or welded on by applying an oxy-hydrogen flame to bar lead.[40] In the latter case a thin skin of lead is first applied by a hot-dipping process, and in the subsequent building-up of the coating, each burned layer is cooled and scraped to remove traces of extraneous materials. The thickness of such a layer after scraping is

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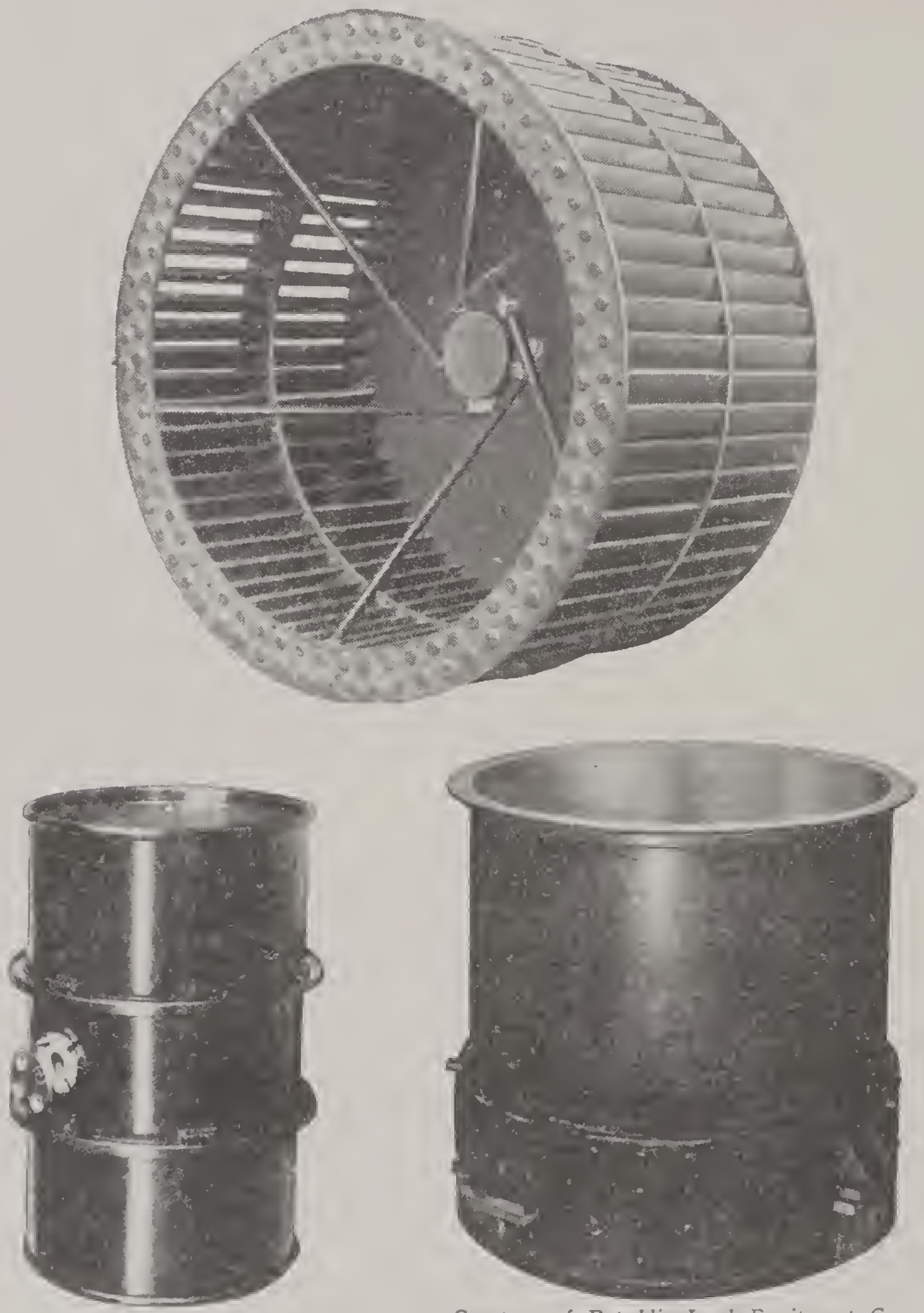
[37] Dean, R. S., Zickrick, L., and Nix, F. C., *Trans. Am. Inst. Mining Met. Eng.*, 73, 505 (1926).

[38] Kurnakow, N. S., and Konstantinow, N., *Z. anorg. Chem.*, 58, 1 (1908).

[39] Bray, J. L., *Trans. Am. Inst. Min. Eng. Inst. Metals Div.*, 124, 199 (1937).

[40] Schlundt, L. R., (Republic Lead Equipment Co.), Cleveland, O. *Private Communication*, July 25, 1938.



Courtesy of Republic Lead Equipment Co.

Figure 50.—Examples of Lead-Coated and Lead-Lined Equipment.

about $\frac{1}{16}$ inch and hence it requires four layers to obtain a coating ¼ inch in thickness. In Figure 50, examples of the types of equipment which may be readily lined or covered with homogeneous lead coatings are shown. Chemical lead is generally employed for linings of this sort, although lead hardened with antimony may be used for coatings of the loose type mentioned in the previous paragraph.

Terne-Plate

This material, often known commercially as "roofing tin," is not infrequently confused with true tin coatings. The name "terne," meaning dull, was originally used in contradistinction to "bright tin," that is, tin-plate. The composition of terne coatings varies within rather wide limits. Commercial terne coatings with a tin content as low as 12 per cent are made, as well as some containing as much as 50 per cent. The one most commonly used in this country, however, is a mixture of 75 per cent lead and 25 per cent tin.

Tin alloys readily with both lead and iron, and hence fulfills the condition necessary for a binder for a lead coating on iron. With lead, tin forms a simple eutectiferous series of alloys; the eutectic contains 63 per cent of tin[41] and melts at 182° C. The solid solubility of tin in lead is much less than formerly supposed; it varies from 2 per cent at room temperature to 18 per cent (approximately) at 150° C.[42] The alloying of tin and iron has previously been discussed.

The manufacture of terne-plate follows quite closely that of tin plate. Much of the light-coated product is made by means of a machine identical in all essential respects with that used for tin-plate of coke grade, the flux used being zinc chloride. The speed at which the sheets are passed through must be reduced in order to obtain as thick a coating as possible, and a higher temperature is required to maintain the bath in a molten state. In order to obtain a coating heavier than 15 pounds per base box, redipping of the sheets after they have passed through this machine is necessary.

A great deal of terne-plate, however, is still made by a process quite similar to the hand-dipping process originally used for tin plate. The essentials of the process are as follows:[43] After the final pickling the clean sheet is kept under water until ready to be immersed in a bath of hot palm oil. After a period of about 20 minutes in the oil, it is immersed in a bath of molten "terne" alloy which is kept covered with an oil layer. From here the sheet is passed into a second pot of molten metal and kept for several minutes. Upon removal from the second pot, the sheets are examined and cleaned, if necessary, before they are dipped into a third pot of metal, this one being of the highest purity of the three used. The sheets are then transferred with as little delay as possible to a bath of hot palm oil where they are allowed to "sweat," the sweating period being determined by the weight of coating desired. If left too long in the hot oil, the coating may be entirely sweated off. The sheets are finally cleaned, as in tin-plate manufacture, in a branding machine. They are finished with either an oil or dry finish. A terne coating, on account of the lead contained, does not have the bright finish of tin plate, no matter how much it may be polished.

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[41] Rosenhain, W., and Tucker, P. A., *Phil. Trans. Roy. Soc.*, 209 A, 89 (1908).

[42] Paravano, N., and Scortecci, A., *Gazz. Chim. Italiana*, 50, pt. 1, 83 (1920).

[43] Camp, J. M., and Francis, C. B., "The Making, Shaping and Treating of Steel," 4th ed., pp. 1016-1023, Carnegie Steel Co., Pittsburgh, Pa. (1925).

During the solidification of the coating, a characteristic surface network or crystal pattern is formed which is analogous to the spangle on zinc-coated sheet. This appearance is known as "mottle" and the size of the network increases with the thickness of the coating. It serves a rather useful purpose, therefore, as an index of the weight of coating.

The finished sheets are carefully inspected and graded. Since a great part of commercial terne-plate is used for roofing and similar purposes for which it is usually necessary to use the entire sheet, without cutting it, very close inspection and grading are necessary. The "prime" sheets must be free from all visible defects and even in the "menders" only such defects as can be remedied by redipping the sheet are permitted. The sheets of the "stripper" grade correspond to the seconds in tin-plate. They may be rerun and converted into primes having a lighter-weight coating. The sheets of "scrap" grade are of no practical use.

The weight of coating on terne-plate is expressed in a manner similar to that used for tin-plate. In this case, the base box consists of 112 sheets, 20 by 28 inches. The weight of coating varies according to the grade, from 8 to 40 pounds per base box. One pound per base box is approximately equivalent to 0.00002 in. The following weights of coating have been generally agreed upon by manufacturers, distributors and users:[44] 8, 15, 20, 25, 30, 32, and 40 pounds per base box; the two weights, 12 and 35 pounds per base box, formerly used, have been discontinued.

Most of the sheets used for making terne-plate for roofing purposes are either of the IC weight, approximately 30 U. S. standard gauge, or IX which is approximately 28 gauge in thickness. In the agreement mentioned above it was recommended that no terne-plate lighter than IC in thickness henceforth be manufactured for roofing purposes in 28- by 20-inch sheets, commonly termed "short ternes."

The use of terne-plate for other uses than roofing has recently increased greatly. The material is admirable for deep stamping operations and nearly 40 per cent of the amount manufactured now is used in this manner.[43] Large quantities are used in the manufacture of gasoline tanks. Sheets much larger and heavier than the roofing size are manufactured for such purposes. They are known as "long ternes" by the trade.

Coatings of lead or of lead-rich alloys afford only a mechanical protection of iron against corrosion. Terne-plate of the heavier weights of coating, for example, 25- to 40-pound coatings, however, gives very satisfactory service as roofing material. It is necessary that such roofs be kept painted. Benches and cabinets for chemical laboratories are often fabricated from terne-plates or lead-coated steel and finished with an acid-resistant paint. The excellent paint-holding properties of such coatings compensate for some of the possible shortcomings which might be expected of coatings of this kind. The resistance of lead coatings to corrosive attack by sulfuric acid also makes them valuable for service for which coatings such as zinc are entirely unsuited.

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[44] "Simplified practice recommendation No. 30. Terne-plate," U. S. Bur. Standards, Washington, D. C. (1925)

Electroplated Lead Coatings

The commercial application of lead plating is quite limited. Most of the practical applications of this type of protective coating depend upon the resistance of lead to attack by sulfuric acid. The usefulness of such coatings for protecting steel against an attack of this kind as well as from some of the special chemicals developed for chemical warfare was strongly emphasized by experience during the war,[45] although very considerable study of lead plating had been done before that time.[46]

Lead can be electrolytically deposited rather easily from a number of solutions but, largely on account of its tendency to form "trees" when deposited from certain solutions, the baths used commercially are limited to three[4] which are rather complex in their composition: the fluosilicate, the fluoborate, and the perchlorate solutions of lead. An addition of some substance such as glue is practically always necessary in order to ensure a dense impervious coating. The fluosilicate bath[47] is composed of lead fluosilicate ($PbSiF_6$) and "free" fluosilicic acid in varying proportions to give a fluosilicate radical concentration of about $2N$. The range of "free" acid used is from 0.25 to $1.2N$. The fluoborate solution[48] is prepared by mixing hydrofluoric and boric acids and then adding basic lead carbonate to the mixture. Satisfactory thick deposits may be obtained from plating solutions in which the lead content is $2N$ and the total fluoboric acid $3N$, operating at a current density of 3 amperes per square decimeter (28 amp./sq. ft.). The perchlorate bath[46] consists of basic lead carbonate dissolved in perchloric acid. The range of concentration usually employed is about 0.4 to $0.6N$ in lead and 0.2 to $0.4N$ in free acid. Alloys of lead and tin may be electrodeposited from fluoborate solutions[49] and have been used for the inside of air-flasks for naval torpedoes.

Corrosion Resistance of Lead Coatings

Porous or very thin lead coatings do not provide satisfactory protection to steel in acidic and neutral environments owing to the development of pinhole rusting. This action is less pronounced and may not occur under mildly alkaline conditions. The thickness of coating required to insure continuity and freedom from pores or bare spots depends upon the coating process employed, plated coatings being the most dense and sprayed coatings the most porous. Hot-dipped coatings are generally not free from pores. Slightly porous coatings may be improved very materially by slightly working or burnishing the surface. Lead linings which are usually at least 0.25 inch are of course non-porous.

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[45] Mathers, F. C., *Metal Ind. (N. Y.)*, 13, 184 (1915); Reeve, A. G., *Trans. Am. Electrochem. Soc.*, 35, 389 (1919).

[46] Mathers, F. C., *Trans. Am. Electrochem. Soc.*, 23, 153 (1913).

[47] Betts, A. G., "Lead Refining by Electrolysis," New York, John Wiley & Sons, 1908.

[48] Blum, W., Liscomb, F. J., Jencks, Z., and Bailey, W. E., *Trans. Am. Electrochem. Soc.*, 36, 243 (1919).

[49] Blum, W., and Haring, H. E., *Trans. Am. Electrochem. Soc.*, 40, 287 (1921).

Electroplated lead coatings 0.004 inch in thickness have been found to give excellent protection to iron and steel exposed to the atmosphere.[50] It seems likely that a thickness of 0.003 inch will usually be pore-free and therefore adequate for ordinary outdoor service. For chemical equipment plated coatings 0.05 inch or greater [51] in thickness are desirable.

Sprayed coatings of lead are readily applied, and as is the case for other metals applied by spraying it is customary to use relatively thick coatings of lead. It has been recommended [52] that coating thicknesses of 0.2 millimeter (0.0078 inch) be employed for prevention of the rusting of steel in the atmosphere, 0.3 to 0.4 millimeter (0.012 to 0.016 inch) for resistance to sea-water and not less than 2.0 millimeters (0.078 inch) for dilute sulfuric acid. Usually lead linings of substantially greater thickness are used in the chemical and petroleum industries.

Lead coatings which are substantially pore-free are resistant to corrosion in the atmosphere because of the formation of a superficial oxide film, relatively impervious in character, which may preserve the metal and therefore protect the underlying ferrous base for long periods of time. Upon injury to the coating, this protective film repairs itself. Usually lead-coated materials will stand severe deformation without noticeable damage to the protective quality of the coatings. The softness of the metal does impose some limitation, however, on the use of lead coatings on hardware and other articles subject to considerable mechanical abuse.

The corrosion resistance of lead to many chemicals, such as sulfuric and hydrochloric acids, brines, etc., has given rise to the use of heavy lead linings in tanks, pipes, pumps and other equipment used in the manufacture and storage of such products. One of the most important single commercial applications of lead plating is for the fittings of storage batteries. Lead plating has also been recommended [48] for lining the copper shells of the ordinary hand fire-extinguisher and for lining flues for conducting the waste gases from gas heaters. In lead-lined fire-extinguishers it has been found [53] that the addition of one ounce of sodium phosphate per gallon of water inhibits the corrosion of both the lead coating and any exposed areas of steel; sodium silicate has been found effective for the same purpose.

The use of lead for water pipes, at one time quite extensive, and the fact that this metal is generally corroded less rapidly by soils than iron and steel, have led to the consideration of lead coatings for pipes used underground. Accordingly, lead-coated pipe specimens were included in the soil corrosion test started by the National Bureau of Standards in 1922. Specimens of steel pipe 6 inches in length and 1.5 inches in diameter with hot-dipped lead coatings of about 0.001 inch in thickness were buried in

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[50] Kurrein, H., *Werkstattstechnik*, **26**, 458 (1932).

[51] Krause, H., *Feinmechanik Präzison*, **40**, 106 (1932).

[52] Forstner, H. M., *Oberflachentechnik*, **11**, 173 (1934).

[53] Hewlett, *J. Soc. Chem. Ind.*, **54**, 1094 (1935).

47 soils of diverse character. Actual measurements of coating thickness showed that there was considerable variation in thickness over the pipe. The results obtained at the end of approximately ten years are given in Table 25[54] which includes for comparison the corrosion rates obtained for steel pipes of the same dimensions and specimens of lead cable sheath-

Table 25.—Corrosion of 1½- by 6-inch Lead-coated Pipe Exposed for Approximately 10 Years.

		Rates of loss (oz./ft.^{2}/yr)			Rates of maximum penetration (mils/yr)		
Soil	Soil type	Lead-coated steel	Bare steel [1]	Lead cable sheath [1]	Lead-coated steel	Bare steel	Lead cable sheath
1	Allis silt loam	0.529	0.80	0.173	11.9	5.8	8.1
2	Bell clay	.102	.49	.067	4.0	6.7	1.8
3	Cecil clay loam	.066	.43	.059	3.6	4.5	1.4
4	Chester loam	.239	.52	.177	7.0	6.8	4.0
5	Dublin clay adobe	.597	.45	.135	6.9	3.1	3.8
6	Everett gravelly, sandy loam...	.096	.08	.025	2.0	1.4	0.8
7	Unidentified silt loam	.207	.37	....	7.0	2.5	...
9	Genesee silt loam	.080	.43	....	5.0	4.5	...
10	Gloucester sandy loam	.163	.36	.088	6.5	3.2	1.2
11	Hagerstown loam	.071	.16	.034	3.4	4.9	1.2
13	Hanford very fine sandy loam	.064	....	....	5.4	...	...
14	Hempstead silt loam	.036	.39	.049	4.2	7.1	1.7
15	Houston black clay	.052	.65	.036	3.2	4.4	2.2
17	Keyport loam	.379	.77	.028	4.7	3.3	1.7
18	Knox silt loam	.046	.23	.016	4.6	3.2	1.1
20	Mahoning silt loam	.224	.52	.268	5.3	5.5	4.1
22	Memphis silt loam	.192	.61	.085	7.3	6.6	1.2
24	Merrimac gravelly, sandy loam	.033	.12	.015	2.2	2.1	1.5
27	Miller clay	.231	.63	.067	5.6	4.9	2.4
28	Montezuma clay adobe	.314	1.75	.069	7.8	15.1	0.9
29	Muck	.689	1.61	.343	6.3	12.0	.9
31	Norfolk sand	.028	.22	.022	1.5	2.5	.5
32	Ontario loam	.072	.32	.028	5.2	4.3	1.5
33	Peat	.537	1.22	....	7.7	8.9	...
35	Ramona loam	.011	.09	.017	(2)	0.4	2.3
36	Ruston sandy loam	.032	.24	.032	1.8	3.9	1.1
37	St. Johns fine sand	.202	.58	....	6.4	5.6	...
38	Sassafras gravelly, sandy loam	.053	.22	.025	3.4	2.5	1.7
40	Sharkey clay	.191	.56	....	6.2	6.6	...
41	Summit silt loam	.051	.45	.039	5.8	7.6	1.5
42	Susquehanna clay	.092	.95	....	4.6	7.1	...
43	Tidal marsh	.726	1.47	.019	18.8	8.7	1.0
45	Unidentified alkali soil	.198	.79	.021	9.2	6.9	1.7
46	Unidentified sandy loam	.033	.37	.015	4.5	8.8	1.0
47	Unidentified silt loam	.184	.23	.122	6.1	2.4	5.7

[1] Bessemer steel pipe 1½ by 6 inches and commercial lead cable sheath in sheets 20¾ by 3½ by 0.112 inch removed from sites at the same time the lead-coated specimens were removed, were buried, in most cases, 1 or 2 years longer. The figures given are the averages from 2 specimens in the case of the steel and 1 specimen in the case of the lead sheath. The penetration of the sheath was determined by averaging 2 pits, each of which was the deepest on one side of the specimen. These pits were, of course, somewhat deeper than would be expected on specimens of the same exposed area as that of the pipe.

[2] No pits.

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[54] Logan, K. H., and Ewing, S. P., *Nat. Bur. of Standards J. Research*, 18, 361 (1937).

ing (approximately 21 by 3.5 by 0.1 inches in size) buried in the same soils. The figures given in the table are the averages of two specimens, except in the case of cable sheath of which one specimen was used.

It will be observed that severe pitting of lead-coated specimens occurred in several soils in which the attack on commercial lead cable sheath was very mild. The generally greater rate of corrosion of lead coatings as compared with lead sheath suggests that the porosity of the coating may accelerate attack in soils much as it does in many other environments. The weight losses are seen to be greater in all instances for bare steel than for the lead-coated specimens, although this is not true for pit-depth. In a later comparative test [54] of lead-coated and bare steel specimens conducted by the Bureau of Standards for a period of only 2 years, it was found that the coating reduces corrosion in the early stages, but that after the coating becomes penetrated the rate of penetration of the steel is often accelerated. From a knowledge of the character of the soils used in these tests it has been deduced that lead coatings show up to the best advantage and are of some value in reducing corrosion in soils which are well drained and of high resistivity. Incidentally the coatings of two different manufacturers were similar in behavior in these soil tests.

Evidently the character of the soil is of considerable importance in determining the corrodibility of lead coatings. It has been shown in other studies[55] that the nature of the soil is more influential on the rate of corrosion than is the composition of the lead alloy.

The mechanism of corrosion in soils is a complex matter. The physical structure of soils, the size and adsorptive capacity of soil particles, permeability to air and moisture, the oxygen and carbon dioxide content of soil air, and the chemical composition of soluble acids and bases present in the soil are variables which must be taken into consideration in soil corrosion reactions. Much of the corrosion of lead, and presumably of lead coatings, which takes place in soils would seem to occur by means of the operation of differential aeration cells produced by contact of the metal surface with soil particles and aggregates. Studies [56] of lead specimens buried in pure sands have shown that relatively large particles are the most effective in producing differential aeration, and that on the other hand particles of colloidal size may even provide protection against corrosion. It will be borne in mind that the occurrence and nature of the corrosive action depends largely upon the effect of the constituents of the environment upon the operation of the corrosion cells. That is, the metal, as explained in Chapter 1, may either corrode or develop a more or less protective film, depending upon whether corroding or protective constituents are preponderant. In the case of lead in soils, the principal corroding elements are oxygen, nitrates, chlorides, alkalies and organic acids and the principal protective agents, silicates, sulfates, carbonates, colloidal substances and certain organic compounds.[55] Usually soils contain varying proportions of most of these substances and consequently the character of corrosion may depend upon the ratio of the concentrations of corroding to protective constituents.

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[55] Burns, R. M., *Bell Sys. Tech. J.*, 15, 603 (1936).

[56] Burns, R. M., and Salley, D. J., *Ind. Eng. Chem.*, 22, 293 (1931).

Finally, to return to the question of the practical value of lead coatings for the protection of iron and steel underground, it is evident from the results given in Table 25 that in certain soils lead coatings are of definite advantage. However, the results of this test scarcely encourage the general use of lead coatings for protection against soil corrosion.

Aluminum Coatings

Aluminum is used as a protective coating for iron and steel and for alloys of aluminum, such as Duralumin, which in ordinary environments are susceptible to corrosion. An important application of aluminum is in the prevention of oxidation of ferrous metals at elevated temperatures. As judged from its markedly electronegative potential, aluminum coatings would be expected to provide cathodic protection to iron at pores or other flaws in the coating which expose the underlying metal. However, owing to the fact that aluminum reacts avidly with oxygen, a superficial oxide film, which is relatively inert and confers an apparent nobility upon the metal, is formed in ordinary environments. In consequence, aluminum offers little if any electrochemical protection to ferrous metals except in chloride solutions; its virtue as a protective metal lies principally in the inherent corrosion resistance of the oxide film which forms on its surface. A further and marked increase in the protective quality of the surface film on aluminum is obtained by anodic oxidation of the metal in a suitable solution, and this process is described in greater detail in Chapter 16.

Coatings of aluminum may be applied by hot-dipping, by cementation, by metal spraying and by mechanical methods. Aluminum may be electrodeposited successfully from non-aqueous solutions,[57] but the process has not as yet attained commercial importance.

Hot-Dipped Aluminum Coatings

Aluminum alloys very readily with iron; hence the fundamental condition for successful coating by hot-dipping is fulfilled. Iron and aluminum are completely miscible in the molten state. In aluminum-rich mixtures, the iron precipitates from the solution, upon solidification of the eutectic (655° C.) as the compound $FeAl_3$ (41 per cent iron). The solubility of iron in solid solution in aluminum is almost nil. Aluminum-rich alloys of the series, up to 41 per cent of iron, have a structure consisting of a matrix which is essentially pure aluminum, embedded in which is a hard, brittle constituent, the compound $FeAl_3$. On the other hand, aluminum is readily soluble in iron, as much as 35 per cent of aluminum being retained in solid solution in α-iron.[58]

Success in the hot-dipping of iron in aluminum is attained with difficulty and only after special preparation of the surface of the iron. Much of the difficulty is to be attributed to the tenacious film of aluminum oxide which forms so readily, and goes to the iron-aluminum interface in the dipping operation. Another factor of importance is the large amount of iron-aluminum compound which forms. This compound ($FeAl_3$) is brittle and should not exceed 0.01 mm. (0.00039 inch) in thickness if the coating is to possess satisfactory mechanical properties.[59] The thickness of the layer increases more rapidly with increasing bath temperature than with increasing time of immersion.[60] In preparing the iron surface for hot-dipping it is essential that all oxide (which interferes with diffusion) be removed; and one method of accomplishing this result is by immersion in molten salt mixtures. Many other methods have been proposed for overcoming the obstacles inherent in the process. For example, a thin layer of cadmium may be deposited on the iron surface and the part preheated before immersion in molten aluminum.[61] Presumably in this case the cadmium vaporizes permitting access of molten aluminum to the clean iron surface in the absence of air. In a somewhat similar process [62] tin- or zinc-coated steel is passed into molten aluminum and the previously coated surfaces mechanically abraded during immersion. Steel strip has been coated with aluminum by first fluxing in zinc-ammonium chloride, and then passing the strip through molten lead into the aluminum bath, the fluxing and dipping operation both being carried out in a reducing atmosphere.[63] In the process most recently developed [64] steel wire or sheet is degreased and pickled in an alkali or acid solution, then heated to about 600° C., fluxed by passing through a concentrated solution of boric acid or borax, heated in hydrogen at a temperature in excess of 732° C. (usually 900-1000° C.) and then passed into the molten aluminum bath which is maintained in a hydrogen atmosphere. Finally, the sheet is wiped. The increased hydrogen absorption in the higher temperature range is said to decarburize the steel surface and saturate it with hydrogen. In coating wire by this process at speeds of 10 to 50 feet per minute, the thickness of the $FeAl_3$ layer does not exceed 2 or 3 ten-thousandths of an inch. It is understood that this process is in successful commercial use.

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[57] Blue, R. D., and Mathers, F. C., *Trans. Electrochem. Soc.*, **69**, 529 (1936).

[58] Kurnakow, N., Urasow, G., and Grigorjew, A., *Z. anorg. Chem.*, **125**, 207 (1922).

Calorizing

Calorizing is the trade-name for the cementation of a metal surface by means of aluminum. The process was developed at the Research Laboratory of the General Electric Company [65] and is intended primarily as a means of protecting iron from oxidation at elevated temperatures rather than from the more familiar type of corrosion. Usually the depth of penetration of aluminum is from 0.005 to 0.04 inch, the iron-alloy layer containing about 25 to 35 per cent aluminum.

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[59] Zeerleder, A. V., *Korr. Metallschutz*, **12**, 275 (1936).
[60] Röhrig, H., *Z. Metallkunde*, **26**, 87 (1934).
[61] Sutton, H., *Brass World*, **25**, 287 (1929).
[62] Uyeno, S., German Patent 265,248 (May 24, 1912).
[63] Dellgren, K., German Patent 632,993 (June 5, 1936); French Patent 743,843 (April 7, 1933).
[64] Fink, C. G., U. S. Patent 2,082,622 (1937).
[65] Ruder, W. E., *Trans. Am. Electrochem. Soc.*, **27**, 253 (1915).

The method is quite similar to that of sherardizing. The articles to be treated are packed in a drum in a mixture of powdered aluminum, aluminum oxide and a small proportion (from 1 to 5 per cent) of ammonium chloride. The drum is slowly rotated as it is being heated and an inert atmosphere, usually of hydrogen, is maintained within it. The aluminum content employed in the process may vary from 5 to 50 per cent according to the service to which the treated piece is to be put. For steel and iron a calorizing temperature of 850 to 950° C. has been recommended, and for copper and brass parts, 700 to 800° C. The rate of diffusion of aluminum into iron rises abruptly at the A_3 point (906° C.).[66] The purpose of the alumina is to prevent coalescence of the particles of aluminum, as the temperature used is very considerably above that of the melting point of aluminum (660.2° C, 1220° F.). The aluminum and the chloride must be renewed from time to time as the mixture is used.

The calorizing process may be carried out by using steel previously coated with aluminum by the hot-dipping method.[67] Upon heating, the aluminum diffuses into the underlying metal, producing a coating which is essentially the same as that obtained by the original calorizing method, although thinner and less protective.

In addition to utilizing the hot-dipping process as a part of the calorizing treatment, various other modifications have been proposed. For example, if iron is placed in an inert or reducing atmosphere containing dry aluminum chloride gas at a temperature of 750-1100° C., metallic aluminum is deposited, replacing the iron, atom by atom, according to the reaction:[68]

$$\underset{\text{Vapor}}{2AlCl_3} + \underset{\text{Solid}}{3Fe} \longrightarrow \underset{\text{Vapor}}{3FeCl_2} + \underset{\text{Solid}}{2Al}$$

The aluminum coating obtained by this process is essentially the same in appearance, structure and properties as that made in the regular calorizing process. It is possible to use illuminating gas, ammonia or ammonium chloride instead of hydrogen in this process.

Considerable advantage may be gained by spraying with aluminum, by the metal-spraying process, parts to be used at high temperatures, such as furnace grate bars and other furnace parts.[69] When heated in the presence of air, such coatings form a tough, adherent oxide layer; alloying with the base metal also occurs. It may be considered, therefore, that a calorized layer is produced. The life of such sprayed aluminum coatings is very much less than that of the regular calorized product, but likewise the initial cost and the cost of renewal are correspondingly less.

[66] Kase, T., Kinzoku no Kinkyu, **12**, 66 (1935).

[67] Howe, G. H., and Brophy, G. R., *Gen. Elec. Rev.*, **25**, 267 (1922).

[68] Martin, E. D., *Doctor's Thesis Univ. Nancy* (1924); *Cournot, J., Rev. Métal*, 22, 139 (1925); "Metal Coating Processes," *Calibron Notebook No. 4* (1937), Calibron Products, Inc., West Orange, N. J.

[69] Hopfelt, R., *Z. Ver. deut. Ing.*, **69**, 411 (1925).

The aluminum deposited during calorizing alloys with the basis metal. The outer hard, rough, porous layer of the coating formed consists largely, in the case of iron, of the aluminum-rich compound, $FeAl_3$, and on account of its porosity affords little if any protection to the treated metal. Beneath the outer layer is a region which is considered to be a solid solution of aluminum in the basis metal. It is to this layer, the structure of which is shown in Figure 51, that the characteristic behavior of a calorized metal is to be attributed.

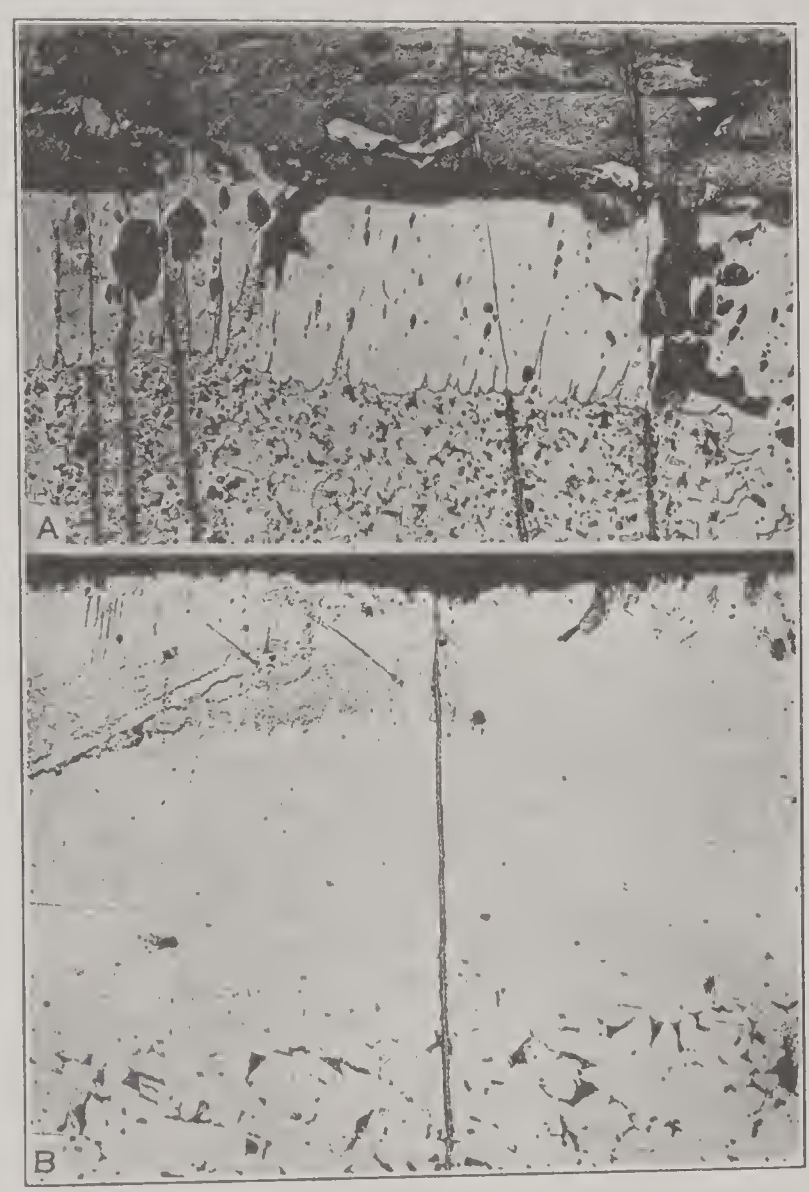

Figure 51.—Structure of an Aluminum Coating on Steel, ×100. Etchant, Alcoholic Solution of Nitric Acid.

A. The coating was formed by dipping in molten aluminum. It consists of two layers, the outer soft one of aluminum (upper part), and a hard alloy adjacent to the steel. The scratches were drawn for purpose of showing the relative hardness of the layers.

B. Coating on a steel rod "calorized" by the commercial powder method. The coating consists of a solid solution of aluminum in iron. By heating A, a coating similar to B would be produced.

The calorizing treatment is especially to be recommended as a protection against oxidation at high temperatures. In Figure 52[65] are given relative rates of oxidation of iron in the treated and untreated condition at 800 °C. and 1000° C. (1470 and 1830° F.), and it will be observed that calorizing exerts a marked retardation on the rate of gain in weight. The pronounced difference in scaling between calorized and untreated steel pipe, when subjected to high temperature for several hours, is shown in Figure 53.[70]

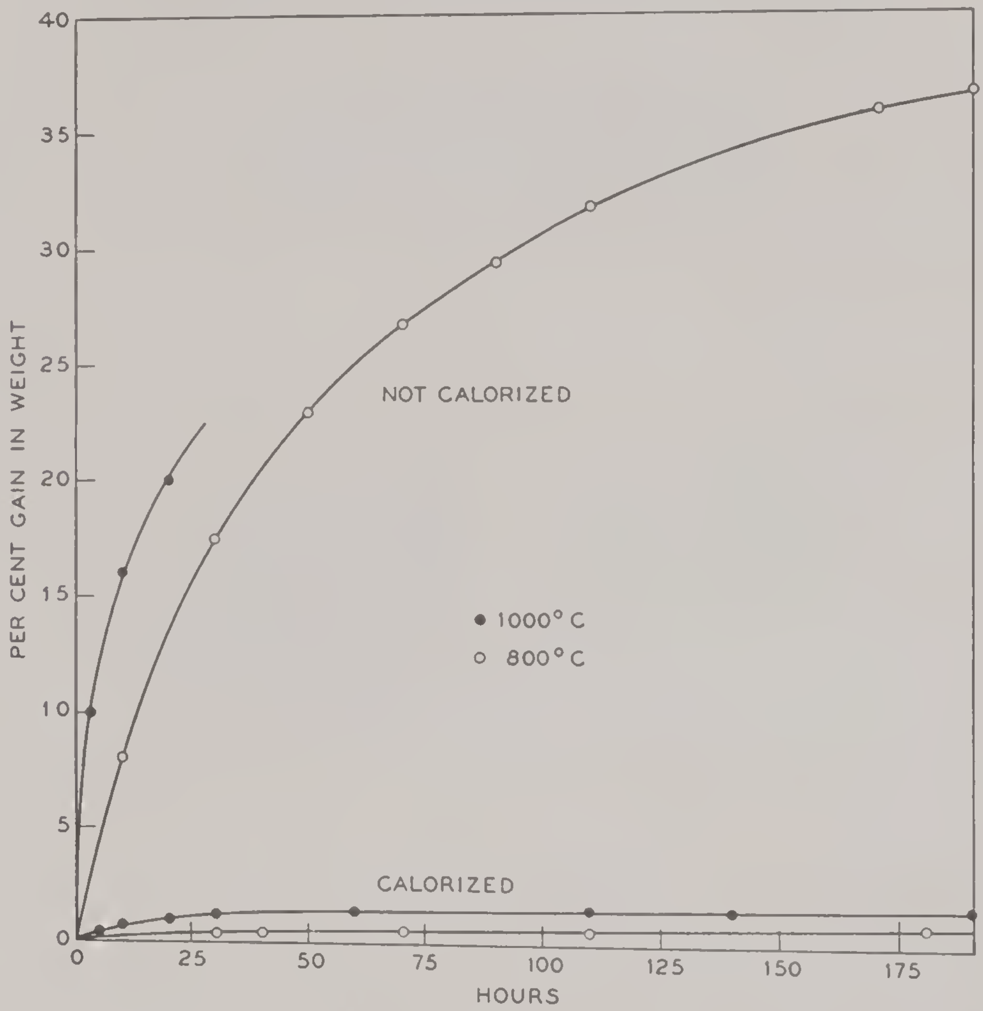

Figure 52.—Rate of Oxidation of Calorized and Uncalorized Iron.[65]

Most of the resistance to oxidation at high temperatures shown by calorized metal can be attributed to the tenacious coating of aluminum oxide which readily forms in the early stage of the heating and prevents further oxidation of the underlying metal. The calorized coating when first put on is quite thin, being only 0.001 to 0.004 inch in thickness. Upon heating, however, the aluminum diffuses deeper into the metal and the coating becomes thicker, but of necessity, has a lower average aluminum content. This factor is of importance as it limits the temperature at which calorized metals may be used to best advantage. If the outer protective layer of alumina becomes broken after the article has been used for a time it cannot be renewed as the aluminum content of the underlying layer has been lowered too much as a result of diffusion. Under these circumstances deterioration of the entire article may result in a short time.

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[70] Allison, H. B. C., and Hawkins, L. A., *Gen. Elec. Rev.*, 17, 947 (1914).

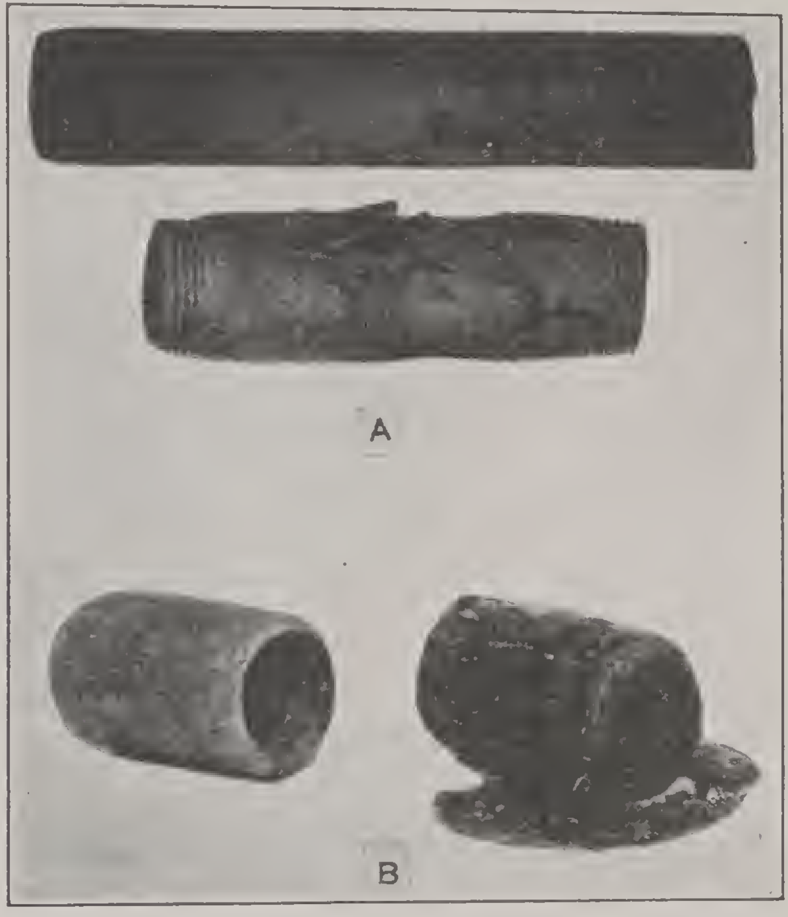

Figure 53.—Appearance of Calorized and Uncalorized Steel Pipe after Heating.[70]

A. 900° C. (1652° F.) 8 hours.
B. 800° C. (1472° F.) 100 hours.
The uncalorized pipe in each case shows pronounced scaling.

It has been estimated[71] that the life of calorized iron below 900° C. (1650° F.) should be almost unlimited; if it is used at 900 to 980° C. (1800° F.), the probable maximum life will be 20 times that of an untreated piece, while if the service temperature is 980 to 1100°C. (2010° F.), the life may be 5 times that of an untreated piece.

Calorized metals will not stand severe deformation without damage to the coating. On iron heavy calorized coatings are sufficiently tough to stand about 5 per cent elongation. Calorized iron is resistant to sulfurous gases and to fused salts at high temperatures, but is corroded by aqueous solutions of mineral acids.[72] Calorizing has found an important application in the oil-refining industry[73] in equipment, such as tube stills for cracking and topping, as well as valves, retorts, and condenser parts. In addition to its use for furnace parts, such as conveyors, stokers, roasters, rotary dryers, kiln parts, carburizing and heat-treatment boxes, and pyrometric equipment, important applications are being made[74] in Diesel engine construction, in the carbon and coke industry, as well as many relatively minor miscellaneous fields where resistance to oxidation and sulfur attack at high temperature is involved.

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[71] Cournot, J., *Rev. Métal*, 23, 219 (1926); *Compt. rend.*, 182, 696 (1926).
[72] Sayles, B. G., "Am. Soc. Met. Handbook," 1938.

Mechanically Applied Aluminum Coatings: "Alclad" Products

Although sheet steel has been coated with aluminum by a mechanical or welding method the product has not been of commercial importance. On the other hand, the coating of aluminum alloys with commercially pure aluminum, or other aluminum alloys as mentioned in Chapter 3, has become an important method for protection of these alloys against corrosion. These products are designated by the American producer as "Alclad" alloys. They are made by casting an ingot of an alloy, such as Duralumin, in a steel mold lined with sheet aluminum or aluminum alloys.[75] Usually the mold is water-cooled or chilled to prevent excessive diffusion of the molten alloy into the aluminum. The aluminum-coated ingot produced in this manner is rolled to suitable dimensions without fracture of the coating, the initial ratio of the thicknesses of sheet metal and alloy being maintained.

"Alclad" aluminum alloys have found wide application in the aircraft industry and in other fields where it is essential that alloys of the Duralumin type be effectively protected against corrosion. In the construction of airplane fuselages it is common practice to employ an "Alclad" alloy in the form of sheet stock and formed supporting ribs. The shell of the all-metal dirigible ZMC-2 consists of "Alclad" 17S-T having a wall thickness of 0.0095 inch (0.24 mm.), and it has shown no loss in properties after more than five years' service.[76] It is of interest to note that the coating metal or alloy is so selected as to be anodic to the core alloy and in that way to furnish electrochemical protection to exposed edges or portions of the core material.

Corrosion Resistance of Aluminum Coatings

Atmospheric exposure tests of aluminum-iron couples conducted under the auspices of the American Society for Testing Materials in nine localities have indicated[77] that aluminum provides little if any electrochemical protection to bare iron at cracks or flaws in the coating. While there was evidence in this test of slight cathodic protection to iron in atmospheres high in chlorides (at La Jolla, California and Key West) there was practically no galvanic activity in rural and urban localities such as State College, Pa., and Rochester, N. Y., respectively. These results are consistent with observations[78] of the behavior of fractured sprayed aluminum coatings on steel exposed to a rather hard city water and to a 0.5N sodium chloride solution. In the first case the exposed iron surface rusted, but in the salt solution the adjacent aluminum coating cathodically protected the bare iron from corrosion. It would appear that destruction of the oxide film on aluminum by means of chlorides permits the aluminum-iron couple to function, corroding aluminum and protecting iron.

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[73] Wilson, R. E., and Bahlke, W. H., *J. Ind. Eng. Chem.*, **17**, 355 (1925).

[74] Farr, A. V., *Iron Age*, **107**, 251 (1921).

[75] Dix, E. H., U. S. Patent 1,865,089 (1932).

[76] Frary, F. C., *Trans. Electrochem. Soc.*, **70**, 131 (1936).

[77] Hippensteel, C. L., "Symposium Outdoor Weathering of Metals and Metallic Coatings," *Am. Soc. Test. Mat.*, p. 99, (1934).

Sprayed aluminum coatings employed in industry are usually from 0.006 to 0.010 inch in thickness, and for severe exposures even 0.015 inch is recommended. Aluminum coatings applied by hot-dipping, like coatings of zinc and tin produced by this method, may be expected to be porous in thicknesses under 0.001 inch. On "Alclad" alloys the pure aluminum layer on thin sheet (0.010 inch) may be only 0.00055 inch in thickness, yet it possesses a high degree of continuity. It is of interest to note, as has been previously mentioned, that the exposed edges of the alloy layer of "Alclad" sheet do not corrode, owing to the fact that the coating is sufficiently anodic to the alloy to induce cathodic protection.[79]

Upon exposure to the atmosphere freshly abraded aluminum rapidly forms an impervious oxide film of the order of a millionth of a centimeter in thickness.[80] After the first few days of exposure the weight-increment curve becomes parallel with the time axis. That is, after 10 to 14 days, the primary film ceases to thicken. The self-healing and inert character of this film provides considerable resistance to ordinary atmospheric corrosion. After long periods of exposure, there is evidence of subsidiary increases in weight of aluminum test specimens which may be due to the repair by oxidation of fissures or cracks which have developed in the primary film. In any case, the rate of corrosion eventually attains a very low value.[81] It has been shown,[82] for example, that although aluminum wire lost approximately 12 per cent in tensile strength and 49 per cent in elongation in the first eight years of exposure to the London atmosphere there was no further loss in these properties in the succeeding 15 years. More recent tests[83] on Duralumin-type alloys have shown that corrosion is practically self-stopping within a few weeks or months depending upon the character of the exposure, and that the depth of penetration is independent of the thickness of the section. It is evident that aluminum coatings should be of sufficient thickness to take advantage of the self-stopping

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[78] Evans, U. R., *J. Inst. Metals*, 40, 99 (1928).

[79] Edwards, J. D., and Taylor, C. S., *Trans. Am. Electrochem. Soc.*, 56, 27 (1929).

[80] Vernon, W. H. J., *Trans. Faraday Soc.*, 23, 113, especially 150 (1927).

[81] Dix, E. H., *Proc. Am. Soc. Test. Mat.*, 33, pt. 2, 405 (1933); see also discussion of same paper by Rawdon, H. S., and Mutchler, W. H., *ibid.*, 414.

[82] Wilson, E., *J. Inst. of Elec. Eng.*, 69, 89 (1930).

[83] Dix, E. H., *Proc. Am. Soc. Testing Materials*, 33, pt. 2, 405 (1933); Rawdon, H. S., *Discussion*, *ibid.*, 414.

Table 26.—Changes in "Alclad" Duralumin Due to Atmospheric Corrosion.

Location	Original Weight	Change in Weight, Grams			Tensile Properties after 6 yrs.		% Change in Tensile Properties		Remarks
		1 yr.	3 yrs.	6 yrs.	Tensile Strength	Elongation (%)	Tensile Strength	Elongation (%)	
Pittsburgh No. 1	167.76	+0.20	+0.18	+0.12	58 845	17.1	−1.1 (*2.2*)*	−10.0 (*6.3*)*	Samples show some mechanical damage, surface generally dirty and roughened with very fine pattern of hard adherent scale.
	171.26	+0.18	+0.14	+0.11					
Altoona No. 2	167.84	+0.18	+0.14	+0.11	58 965	17.4	−0.9 (*2.0*)	−8.4 (*4.0*)	Samples show some mechanical damage, surface generally dark and dirty and roughened with very fine pattern of hard adherent scale.
	170.64	+0.24	+0.39	+0.47					
New York City No. 4	169.40	+0.35	+0.26	+0.17	59 255	18.9	−0.4 (*2.2*)	−0.5 (*3.5*)	Surface dirty and generally roughened with very fine pattern of hard adherent scale.
	173.25	+0.32	+0.24	+0.16					
Rochester No. 6	169.77	+0.12	+0.29	+0.66	58 245	15.6	−2.6 (*2.4*)	−17.9 (*19.7*)	Dull dirty film speckled with small spots of darker hard adherent scale.
	169.48	+0.11	+0.22	+0.38					
Sandy Hook No. 5	171.53	+0.20	+0.25	+0.14	58 945	18.3	−0.9 (*2.6*)	−3.7 (*3.5*)	Dull dirty film speckled with fine spots of darker hard adherent scale, dark scale along edges.
	173.09	+0.23	+0.26	+0.16					
Key West No. 7	172.96	+0.09	+0.14	+0.20	59 855	18.8	+0.6 (*2.4*)	−1.1 (*4.4*)	About 50 per cent of surface shows metallic luster; remainder, gray thin film with light scale spots resembling bird tracks, heavier scale near edges.
	167.17	+0.07	+0.12	+0.18					
La Jolla No. 9	172.22	+0.62	+0.55	+1.13	59 565	18.6	+0.2 (*2.0*)	−2.1 (*4.4*)	Dull gray thin scale with uniformly distributed mounds of heavier granular scale, 30 per cent of area still shows metallic luster.
	170.88	+0.63	+0.60	+1.14					
State College No. 3	169.45	−0.01	−0.03	−0.05	59 500	17.9	+0.1 (*2.5*)	−5.8 (*6.2*)	Generally discolored but still showing metallic luster, uniformly distributed small light gray spots over the mottled tarnished background.
	171.61	+0.09	+0.07	+0.05					
Phoenix No. 8	170.06	+0.03	+0.01	+0.03	59 080	19.3	−0.7 (*2.7*)	+1.6 (*3.5*)	Metallic luster generally visible over entire surface with a mottled pattern of gray spots, fine black spots uniformly distributed on numbered side.
	168.98	+0.03	+0.01	+0.03					

* Italic figures in parentheses indicate maximum percentage difference due to chance.

action, that is, to provide for the development of an effective surface film, before widespread perforation of the coating occurs.[84]

One of the most extensive tests of the corrodibility of "Alclad" coatings in the atmosphere is that being conducted by the American Society for Testing Materials[85] at nine locations, which embrace a wide range of atmospheres. The results of this test at the end of six years for "Alclad-17ST" (Duralumin) 0.032 inch in thickness are given in Table 26. The pure aluminum layer on this stock is approximately 0.00176 inch in thickness.

It will be observed that after six years the alteration in physical properties is insignificantly small. The percentage change in tensile properties in almost all cases is shown to be less than the maximum change due to chance (italic figures in parentheses). The weight-increments over the period also are small and of the same order as those observed on commercial aluminum exposed in the same test. In contrast to these findings bare Duralumin also included in this test showed pronounced loss in tensile properties except in the two rural stations, State College, Pa., and Phoenix, Arizona. From these results it is clear that the aluminum coatings in this test are still intact and are providing adequate protection to Duralumin at the end of six years.

The resistance of calorized coatings to sulfurous atmospheres has been mentioned previously. Pure aluminum surfaces, similarly, resist corrosion satisfactorily in industrial atmospheres. Aluminum wire has been found superior in performance to copper wire in sulfur dioxide atmospheres prevailing in the neighborhood of smelters which treat sulfur-bearing ores. Seaside atmospheres on the other hand are relatively more active in stimulating corrosion of aluminum, owing to the tendency of chlorides to break down, penetrate or otherwise displace protective oxide films. "Alclad" Duralumin 0.064 inch in thickness has however shown satisfactory resistance to 20-per cent sodium chloride spray for periods up to eight years. This heavy-gauge "Alclad" sheet is employed for airplanes which are subjected to salt spray at intervals, but sea planes which experience more severe exposures are commonly constructed of painted "Alclad" sheet.[84] Studies have shown that the most effective painting procedure for marine use is a priming coat of zinc chromate in a synthetic resin vehicle, followed by two or three coats of aluminum paint in the same vehicle.[86] Paint coatings of this type are effective in preventing the corrosion of bare Duralumin and other aluminum alloys, particularly if the alloy surface is first anodically oxidized to provide a good bond for the paint coating.

Aluminum is resistant to distilled water and to ordinary fresh waters whether soft or hard. The presence of heavy metals, particularly copper, tin, lead and nickel, is deleterious, and waters which are high in chlorides or alkaline carbonates are corrosive. Most fresh waters contain silicates, and as in the case of lead, silicate is a protective agent for aluminum in mildly alkaline solutions.

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[84] Dix., E. H., and Mears, R. B., *Mech. Eng. (Am. Soc. Mech. Eng.)* **58**, 784 (1936).

[85] Finkeldey, W. H., *Proc. Am. Soc. Testing Materials,* 38 (1938).

[86] Edwards, J. D., and Wray, R. I., *Ind. Eng. Chem.,* **27**, 1145 (1935).

Numerous investigations have been made of the behavior of aluminum and aluminum coatings, as represented by "Alclad" products and sprayed aluminum, in seawater and salt solutions. It is perhaps sufficient merely to reiterate that aluminum is attacked by halogen salts but not by sulfates and nitrates.[87]

Aluminum coatings of the sprayed, dipped or "Alclad" type are probably unsuitable for protection of underground structures. Soil tests made a few years ago on specimens of sheet aluminum showed that the metal is badly pitted by contact with soil particles—the result, very likely, of differential aeration attack. Calorized coatings on steel pipe included in the Bureau of Standards soil test[54] were pitted at a lower rate than were bare steel specimens buried in the same test. It was found in this test, in which specimens calorized by both the powder and dipping processes were compared, that, while the powder-calorized coating was more effective in reducing pitting, it allowed a greater loss of weight than did the dip-calorized coating.

Miscellaneous Metallic Coatings

Brass Coatings

The simultaneous electrodeposition of copper and zinc to form a coating of brass can be accomplished readily by the use of a cyanide solution of the two metals. In ordinary solutions, for example, sulfates, the difference of potential between copper and its solution (copper ions) varies so greatly from that between zinc and its solution (zinc ions), that the simultaneous deposition of the two metals is impossible. In a cyanide solution of the proper concentration, however, the potentials of the two metals are so nearly the same that copper ions and zinc ions can be discharged at the same time on the cathode, and a layer of brass is thus formed. Examination of the deposit formed by means of the x-ray diffraction method has shown that such a deposit is a true alloy of the two metals and not merely a mechanical mixture of small crystals of copper and zinc.

The essential constituents of a brass plating bath are copper and zinc cyanide and sodium cyanide. Sodium carbonate is sometimes added. The most suitable pH range appears to be 10.7 to 11.0. Cast brass anodes containing 70-80 per cent copper are generally employed and the bath is operated at about 32 to 45° C. (90 to 113° F.) at current densities from 0.2 to 1 ampere per sq. dm. (2 to 10 amperes per sq. ft.). Arsenic trioxide, phenol and ammonia in small quantities are sometimes employed as brightening agents to improve the appearance of the deposit. Steel strip is now coated with brass by annealing a duplex electrodeposit of copper and zinc for 10 to 30 minutes at a temperature between 700 and 1500° F.[87a]

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[87] For a more extended review of the corrosion of aluminum in various media, see reference 84.

[87a] Thomas, C. G. (Thomas Steel Co., Warren, O.), *Private Communication*, October 27, 1938; Rubin, U. S. Patent 2,115,749 (1938).

Brass coatings are used quite extensively on iron and steel articles, especially upon builders' hardware, to give the appearance of solid brass. Such coatings are primarily for appearance. As a rule, they are very thin and afford little protection from atmospheric corrosive agencies. Brass-plated iron and steel articles rust very readily (even when lacquered) when used for out-of-door exposure, because such coatings are usually for decorative purposes and are very thin.

It is claimed [88] that brass is superior to copper as an intermediary layer or undercoating for nickel and chromium, owing to a greater tendency of these metals to adhere to brass. So far as is known, however, brass plating is not commonly employed for this purpose.

Brass plating has come into rather wide use lately to secure satisfactory adhesion of rubber coatings to metal. An important application is in connection with the attachment of rubber tires to steel tire rims where brass plating of the rims has proved to be the most feasible method of obtaining the necessary degree of adhesion of vulcanized rubber to the rim. In contrast to ornamental brass plating, where close control of color is desirable, brass deposited for rubber adhesion requires close control of composition. It has been found [89] that the most suitable range of composition is from 24.4 to 33.6 per cent zinc for the process employed. Deposits of about 0.00002 inch in thickness are generally employed. As would be expected, tarnish films usually reduce adherence. Brass appears to offer no advantage in the adhesion of Neoprene and rubbers vulcanized without sulfur.

Cobalt Coatings

Cobalt was electrodeposited as early as 1842, and it has long been known that the metal could be deposited readily on iron and other common metals. Cobalt ammonium sulfate or cobalt sulfate with sodium chloride may be employed as plating salts. The fact that a cobalt bath could be operated satisfactorily at current densities as high as 16.2 amperes per sq. dm. (150 amperes per sq. ft.)[90] stimulated considerable interest in cobalt plating a few years ago. Although the price of cobalt has been markedly reduced since the beginning of the present century, owing to the discovery of large cobalt ore bodies, the metal is still too expensive to permit commercial exploitation of cobalt coatings. As mentioned in Chapter 9, one of the processes for bright nickel coatings employs anodes containing 18 per cent cobalt and yields a bright deposit which is a cobalt-nickel alloy. Studies have been made of means of increasing the brightness of cobalt deposits.[91] Alloys of cobalt with nickel, and ternary alloys of cobalt, nickel and iron may be readily electrodeposited. Cobalt coatings are bluish-white in color, are somewhat similar to iron and nickel in hardness, and resemble nickel in their microstructure. There has been some controversy concerning the relative corrosion resistance of cobalt and nickel coatings. Although cobalt oxidizes somewhat more readily and is less resistant to weak acids than is nickel, its resistance to atmospheric corrosion appears to be of the same general order as that of nickel.

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[88] Braun, A., *Oberflachentech.*, 12, 39, (Feb., 1935).

[89] Coats, H. P., *Monthly Rev. Am. Electroplaters' Soc.*, 24, 5 (1936).

[90] Kalmus, H. T., Harper, C. H., and Savell, W. L., *Trans. Am. Electrochem. Soc.*, 27, 75 (1915).

[91] Chaybany, A., *Met. Ind. (London)*, 48, 721 (1936).

Tungsten Coatings

Tungsten was first electrodeposited from fused salt baths. For example, smooth, but thin, deposits were obtained from sodium and lithium tungstates containing tungstic acid at temperatures above 1000° C. (1832° F.), operating at 70 to 80 amperes per sq. dm.[92] These deposits, however, have not been of any commercial importance. More recently tungsten has been successfully deposited from aqueous solutions, notably from an alkaline sodium tungstate solution.[93] The bath, consisting of tungstic acid dissolved in sodium carbonate and having a pH value of 12 to 13, is most suitably operated at about 95° C. at current densities from 8 to 10 amperes per sq. dm. (75 to 100 amperes per sq. ft.). The tungsten coating obtained in this process is smooth, hard, highly lustrous and of a bluish-white color. It is, however, very thin, the deposition process apparently ceasing after the deposition of from 0.003 to 0.05 gram of tungsten per square decimeter of surface area. The plating bath after a period of usage appeared to become exhausted and failed to deposit tungsten. Subsequently it was shown[94] that the addition of very small proportions of iron to a tungsten bath, which had been depleted in this manner, tended to restore or regenerate it; and furthermore it was found that deposits could not be obtained from baths made from highly purified salts. This experience and the fact that iron was invariably found in tungsten deposits from ordinary alkaline carbonate, and also phosphate and citric acid baths, led to the conclusion that iron is present in tungsten deposits from aqueous tungsten plating baths.

As would be expected from the foregoing discussion, alloys of tungsten with iron and also with nickel, cobalt, tin and a variety of other elements may be electrodeposited.[95] Coatings of alloys of tungsten with 65 per cent of nickel or tantalum may be plated in various thicknesses. These deposits have a high luster and are similar in porosity to nickel coatings of the same range of thicknesses.

Pore-free coatings of the nickel and tantalum alloys of tungsten show excellent resistance to attack by strong acids, alkalies and salt solutions. As yet, however, these coatings have not attained any appreciable commercial use. Coatings of tungsten, as well as of molybdenum and tantalum, can be produced by cementation on iron and copper alloys. This is readily accomplished by embedding the metal to be coated in the appropriate ferro-alloy at 800 to 1200° C. (1650-2200° F.) in the presence of ammonium chloride vapor.[96] It has been shown also that coatings of boron, tantalum, vanadium, cobalt, uranium, silicon, zirconium, and titanium can be produced on steel by cementation methods.[97] As in the case of chromizing and calorizing, which have been described previously, coatings of the metals mentioned above do not consist of the pure metal, but of a combination of the coating and the basis metal. Although the composition and properties of these coatings have not been studied extensively, it is reported that cemented molybdenum and tungsten coatings are acid-resistant and that zirconium coatings are resistant to oxidation at high temperatures.

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[92] Van Liempt, J. A. M., *Z. anorgan. Chem.*, **122**, 175 (1922); 143, 285 (1925).

[93] Fink, C. G., and Jones, F. L., *Trans. Electrochem. Soc.*, **59**, 461 (1931). Fink, C. G., U. S. Patent 1,885,702, (Nov. 1, 1932).

[94] Holt, M. L., *Trans. Electrochem. Soc.*, **66**, 453 (1934).

[95] Holt, M. L., *Trans. Electrochem. Soc.*, **71**, 301 (1937).

Tantalum Coatings

Tantalum occurs in nature together with the element columbium in a mineral known either as tantalite or columbite, depending upon which of the two predominates in concentration. Both minerals are tantalates and columbates of iron and manganese. Tantalite is obtained from Western Australia and from the Black Hills district of South Dakota, and it occurs in concentrations so low that approximately two and one-half tons of rock are required to produce one pound of tantalum.[98]

The ore is treated chemically to produce tantalum salts from which the metal is obtained in the form of powder by reduction. The methods of powder metallurgy (high pressure and sintering, in this case, in a vacuum) are employed to produce bars from which ductile and malleable sheets of the metal may be obtained.

Tantalum coatings may be applied by metal spraying. Inasmuch as thickness of deposit of from 0.070 to 0.100 inch is required to overcome porosity, the use of sprayed tantalum has been restricted to certain special applications, such as to the shafts of pumps to be used for acids. It is more common in the manufacture of corrosion-resisting equipment to employ what is known as sheet-metal technique. In this process, thin sheets of tantalum are welded to the surfaces of steel and certain other metals. Such coatings are, of course, continuous in character.

Tantalum coatings have come to be used in recent years in chemical equipment employed in the processing of chlorine compounds, and strong acids. Hydrofluoric acid, fluorides, and hot or fuming sulfuric acids attack the metal. At approximately 175° C. tantalum reacts with chlorine.

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[96] Laissus, J., *Compt. rend.*, 182, 1152 (1926).

[97] Laissus, J., *Chim. Ind.*, 29, 515 (1933).

[98] The authors are indebted to the Fansteel Metallurgical Corporation of North Chicago, Illinois, for much of the information given concerning tantalum coatings.

Chapter 11

Coatings of Noble and Rare Metals

History of Gilding and Silvering of Metals

Historically, the first metal coatings were those of gold and silver. Although the idea of ornamentation was always foremost in the minds of the users of such coatings and still remains so, they are, nevertheless, properly to be considered as protective coatings. At the present time gold and silver coatings are used in some instances, although to a very limited extent, primarily as a protection against severe corrosive attack; typical examples are the silver lining of autoclaves, the gold plating of the interior of bomb calorimeters and the gold plating of standard weights and other laboratory equipment. The silver plating of the fixtures used for dispensing soda water and similar drinks is an example of the use of silver plating on a larger scale.[1] Lately the use of silver-lined equipment in the food industry has been extended. Coatings of silver, gold, platinum and palladium are coming to be used for electrical contacts.

The gilding and silvering of metals has been practiced for centuries and many ingenious methods have been developed. The earliest method depended upon the use of gold hammered into foil. This practice was known in Egypt as early as 3000 B. C. Gilding and bronzing by means of finely powdered metal in suspension in a suitable vehicle followed. Fire or amalgam-gilding, which was applicable to silver as well as to gold, was known, at least in a crude form, as early as 300 A. D.[1a] In this method the surface to be coated, usually brass or copper, was first treated with a solution of mercurous nitrate and then rubbed with an alloy consisting of 9 parts of mercury to 1 part of gold. After the surface had been thoroughly amalgamated, the mercury was expelled by means of heat. This could be repeated more than once if a very heavy coating was desired. The use of the mercury insured intimate alloying between coating and base. It is claimed by some that such coatings are much superior to the modern electroplated gold coatings, and the process is still used to a very limited extent.

The method of "close plating"[2] was formerly widely used for producing silver-coated articles and was the immediate predecessor of the fusion method which we know principally as the method for making "Old Sheffield Plate."

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[1] The American Silver Producers Association has in progress an extensive research program directed toward the development of wider industrial use of silver and silver coatings. For a discussion of the properties and industrial uses of silver see: Rogers, B. A., Schoonover, I. C., and Jordan, L., *Nat. Bur. Standard Cir.*, C 412 (1936); Lee, J. A., *Ind. Eng. Chem.*, 28, 1412 (1936).

[1a] Theobald, W., *Ding. Poly. J.*, 328, 163 (1913).

[2] Bradbury, F., "History of Old Sheffield Plate," London, MacMillan & Co., 1912.

In close plating, the finished article was cleaned with ammonium chloride and then dipped into molten tin. A thin foil of silver cut to the approximate size and shape needed was carefully fitted over the article and a hot soldering iron lightly rubbed over it. The tin melted and soldered the silver coating in place, after which the article was burnished and polished. Close plating was applied to articles of rather complex shape including knives, forks and spoons and other tableware, as well as buttons, buckles, snuff boxes, spurs and other articles for personal adornment. Close-plated articles could not be heated; otherwise the tin solder would melt and the coating would strip off. Neither would it withstand very severe corrosive conditions, because blisters formed as a result of corrosive attack beneath the coating. The method is still in use today, however, in a few special cases.

The fusion method of silver plating copper was discovered by Thomas Boulsover about 1743. In brief, this consisted in heating a slab of copper, with a thinner plate of silver in close contact, nearly to the fusion temperature of silver, and subsequent rolling of the composite slab into sheet form. First of all, the slab, which, though described as copper, was an alloy of copper with some zinc and lead, was planed off to a very smooth surface as was likewise the silver plate, the thickness of which depended on the final thickness of silver plating desired. For double-coated sheet both sides of the copper slab were treated. The copper slab and silver plates were pressed firmly together, covered with sheet copper which had previously been dressed with powdered chalk to prevent it from fusing to the silver, bound with iron wire and heated until the silver began to "weep." It was then removed from the furnace, stripped of its copper sheathing, cleaned and rolled into sheet form. From this composite sheet many intricate and complex shapes were worked out, which are known to us as "Old Sheffield Plate." With the discovery and commercial development of the cheaper electrolytic method of silver plating, the fusion method passed out of use.

ELECTROPLATED SILVER COATINGS

The commercial application of the electrodeposition of silver dates from about 1840 with the discovery by John Wright, a young surgeon of Birmingham, England, that a cyanide solution of silver must be used in order to obtain a dense, uniform adherent coating of silver. Cyanide solutions are still used today almost exclusively in the silver-plating industry. These solutions possess many advantages, such as high anode and cathode efficiencies and good plating characteristics over a wide range of solution composition, temperature and current density. The silver cyanide bath is prepared by dissolving silver cyanide in potassium or sodium cyanide, forming thereby a double cyanide. In recent years the sodium salt has come to be largely used for this purpose although the potassium compound is preferable, as it possesses a high conductivity and a wider plating range in terms of current density.[3] The plate from the potassium solution is said to be superior in physical appearance and may be burnished more satisfactorily than that from sodium cyanide.[4] Owing to the poisonous nature of cyanide solutions, many attempts have been made to deposit silver from solutions of other silver salts such as the sulfate, nitrate, fluoride and fluoborate,[5] but the results have been unpromising. Recently, however,[5a] deposits have been obtained from acid complex iodide baths which are said to be equivalent in quality to those obtainable from cyanide baths.

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[3] Egeberg, B., and Promisel, N., *Trans. Electrochem. Soc.*, 59, 287 (1931).

Silver deposits from cyanide solutions have a milky or frosted appearance and may require buffing to secure a bright surface. To overcome this difficulty it has long been customary to add to the plating bath small proportions of carbon disulfide as a brightening agent. More recently it has been shown that the addition of about 1 gram of sodium thiosulfate and 10 cc. of ammonia per liter of plating solution is more effective than is carbon disulfide in producing a bright white silver deposit.[6]

Numerous variations may be necessary in the preliminary treatment of metals to be plated, such as "strikes" and "dips" in various solutions before immersion in the plating bath. Most metals tend to precipitate silver from solution by simple immersion, and this tendency is minimized by "striking" the basis metal at high current densities in solutions of low metallic ion concentrations—usually dilute cyanide solutions. Another method of reducing immersion plating and securing deposits of improved adherence is to flash the metal to be plated with a thin layer of a metallic deposit which shows a lesser tendency to replace silver from solution. There appears to be some advantage in a preliminary copper strike followed by a silver strike in the silver plating of steel surfaces. By this means adherent smooth deposits 0.05 to 0.07 in. in thickness may be obtained.[6a]

Thickness of Silver Plating

It was formerly the custom in describing silver-plated ware to use such designations as "triple-plated," "quadruple-plated," and the like. The use of these misleading terms has now been discontinued by American manufacturers and the weight of silver, for example, per unit of surface area as on a stated number of articles of similar kind and size, is used instead to indicate the thickness of the coating. Table 27 gives the average thickness of the coating on silver-plated tableware as adopted under the NRA and since generally accepted.[7] The Federal Specification Board specifies for all pieces an average thickness of silver of 0.00125 in. This corresponds to 1 troy ounce per square foot. For overlay 0.0018 in. is specified.[7a]

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[4] Mesle, F. C., *Monthly Rev. Am. Electroplaters Soc.*, **15**, No. 10, p. 4 (1928).

[5] Sanigar, E. B., *Trans. Electrochem. Soc.*, **59**, 307 (1931).

[5a] Alpern, D. K., and Toporek, S., *Trans. Electrochem. Soc., Preprint* **74**, No. 14 (1938).

[6] Pan, L. C., *Trans. Electrochem. Soc.*, **59**, 329 (1931).

[6a] Mathers, F. C., and Gilbertson, L. I., *Trans. Electrochem. Soc., Preprint* **74**, No. 30 (1938).

[7] *Metal Ind. (New York)*, **32**, 340 (1934).

[7a] Federal Specification Board Specification RR-T-51a, June 5, 1934.

Table 27.—Average Weight of Coating on Silver-Plated Tableware.

	Teaspoon (Oz. Silver Per Gross)	Dessert Spoon Dessert Fork R.B. Soup Spoon (Oz. Silver Per Gross)	Tablespoon Dinner Fork (Oz. Silver Per Gross)
"A1" or "Standard"	2	3	4
"AA"	3	4½	6
"Double" or "X"	4	6	8
"Triple" or "XXX"	6	9	12
"Quadruple" or "XXXX"	8	12	16

It is also necessary to take into account the thickness of the coating on those portions of plated tableware which are subjected to the greatest wear, such as the back of the bowl of spoons or the tines of forks. It is common practice, for the better grade of tableware, to use a heavier coating on such portions. This is obtained either by use of a silver insert in the "blank," which is later plated, or by a supplementary plating of the desired portions after the article has been given the regular plating. The specification referred to above requires the silver coating to be 0.0012 inch thick on such spots.

Defects in Silver Coatings

The occurrence of red stains on silver-plated articles is sometimes the cause of considerable concern to silver platers. This defect has been shown[8] to arise during the polishing operation; it appears to be related to improper use of the polishing rouge on a surface while still heated by the polishing operation.

"Spotting out" on silver-plated surfaces is another defect. These white spots, which do not appear until some time after the article has been removed from the plating bath, are to be ascribed primarily to inclusion of some of the cyanide in the coating. The exact nature of the defect, however, has not been fully established.

At times difficulty is experienced in polishing silver coatings. The coating in such cases often has a coarse crystalline appearance which is removed with difficulty by ordinary polishing methods. It has been reported that silver may be electrodeposited under certain conditions so that the crystals of the silver form as extensions of the pre-existing crystals of the nickel-silver base metal (compare Figure 46). Such coarsely grained silver coatings cannot be satisfactorily polished by the methods usually employed. It has not been established, however, that this is the only cause for irregularities in the polishing of silver-plated coatings.

Tarnishing of Silver

Silver readily tarnishes upon exposure to industrial atmospheres or indoor air contaminated by the products of combustion of sulfur-bearing fuels. Foods such as onions and eggs, which contain organic sulfur compounds, are also well known to tarnish silver.

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[8] Jefferson, A., *J. Inst. Metals*, 28, 447 (1922).

The tarnish film which forms on silver exposed to the air is composed of silver sulfide and contains no oxide. Even when silver which has been previously oxidized is exposed to the air the film becomes converted into sulfide. The gain in weight of silver with time of exposure to the atmosphere is parabolic in type. This suggests that the process is controlled by diffusion. It has been proposed recently that the tarnishing process is electrolytic in character [8a] and that the rate of tarnishing of silver is probably controlled by the mobility of silver ions, which is unusually high.[8b] The rate of tarnish does not appear to be appreciably influenced by the variation in humidity prevailing indoors throughout the year. Unlike the behavior of many of the base metals, there does not appear to be in the case of silver a critical relative humidity above which the rate of corrosion is abruptly and markedly accelerated.

In appearance tarnish films on silver exhibit the usual range of interference colors. There seems to be little relationship between the appearance of tarnished silver and its electrical contact resistance.

The removal of the tarnish film on silverware may be accomplished by polishing the surface with a fine abrasive or by electrolysis. If, in a solution of sodium chloride and sodium carbonate, both of which are common household materials, a tarnished silver article is placed in contact with a metal, such as zinc or aluminum, it will be detarnished. The base metal serves as anode, the silver as cathode, and by means of cathodic action the silver sulfide is reduced to silver. Silver knives with stainless steel blades should not be subjected to this treatment. There is no appreciable loss of silver in the reduction process. If the silver has been very severely tarnished, the surface after cleaning is dull on account of the thin film of "moss" silver formed by reduction of the sulfide. Buffing may be necessary in such cases to restore the polish.

Attempts have been made to improve the tarnish resistance of silver by the codeposition of another metal. Silver-cadmium alloys were proposed for this purpose [9] but it was found that alloys containing 3 per cent or more of cadmium possess an undesirable yellowish tinge.[10] An electrodeposited silver-cadmium alloy containing about 24 per cent of silver has been recommended for its light-reflecting properties inasmuch as it maintains its reflecting power to a greater degree than does silver when both are tarnished.[11] Alloys of silver with indium may be plated and are claimed to possess superior resistance to tarnish.[12] Silver-lead alloys are said to tarnish more readily than silver alone.[12a] A recent extensive study of the tarnishing of silver and silver alloys[8b] indicates that the most feasible method of preventing tarnish is to provide a surface film of high electrical resistance. This is most successfully accomplished either by the selective oxidation of aluminum or beryllium in silver alloys or by the superimposition of cathodically deposited films of these oxides on pure silver or its alloys.

[8a] Wagner, C., *Z. phy. chem.*, B 21, 25 (1933); 32, 447 (1936); Hoar, T. P., and Price, L. E., *Trans. Faraday Soc.*, 34, 867 (1938).

[8b] Price, L. E., and Thomas, G. J., *J. Inst. Metals*, 63, (1938), (Advance copy).

[9] Proctor, C. H., *Metal Ind. (New York)*, 18, 13 (1920).

[10] Aten, A. H. W., and van Putten, M. F., *Rec. trav. chim. des Pays-Bas*, 44, 861 (1925).

[11] Stout, L. E., and Thummel, W. G., *Trans. Electrochem. Soc.*, 59, 337 (1931).

[12] French Patent 699,068 (1930); Gray, D., Bailey, R. O., and Murray, W. S., U. S. Patent 1,847,941 (1932).

GOLD COATINGS

Gold coatings are applied by electroplating and by gold-filling—a process which resembles that employed in making Old Sheffield plate. Because of the highly electropositive or noble character of gold, coatings of this metal do not afford any electrochemical protection to base metals. The resistance of gold to chemical attack and tarnish makes it a particularly desirable metal to use in highly corrosive environments provided the coating is substantially pore-free. Gold coatings are widely used for certain types of electrical contacts, notably on the electrodes of telephone transmitters.

Gold electroplating solutions usually consist essentially of the double cyanide of gold and potassium. Sodium cyanide may be employed in place of the potassium salt and in some cases a small percentage of sodium phosphate is added to the solution. Gold baths are operated in the temperature range 45 to 80° C. (113 to 176° F.) and at current densities from 0.1 to 0.5 ampere per sq. dm. (1.0 to 5.0 amperes per sq. ft.). By varying the composition of the plating solution, that is, by adding other metals such as silver, copper and nickel, coatings of green, red and white colors may be obtained. These deposits are in reality alloys of gold and the other metal.

Gold can also be plated without the application of an electromotive force external to the plating cell. One such method merely requires setting up a primary battery which uses two solutions; one of them, the gold solution, is kept separate from the second one, sodium chloride, by means of a porous cup. A strip of zinc, the anode of the cell, is immersed in the sodium chloride solution; the article to be plated, either brass or copper, is hung in the gold solution within the porous cup. Electrical contact by means of a wire is made between the two electrodes, that is, the zinc strip and article to be plated. In such a cell, gold from the solution deposits upon the surface of the cathode (article to be plated) when a current is allowed to flow by connecting the anode and cathode by a wire. The deposit is very uniform and adherent. A much simpler method merely requires immersion of the article, brass or copper, in a gold solution of the proper composition. In this case, the article is plated by the passage of a slight amount of copper or zinc into solution and the precipitation of an equivalent amount of gold on the surface. The coating obtained is very adherent but exceedingly thin and the method is used only for small, cheap articles. Such coatings are only a few millionths of an inch in thickness.[13]

[12a] Mathers, F. C., and Johnson, A. D., *Trans. Electrochem. Soc., Preprint* 74, No. 27 (1938).

Electroplated gold coatings are fine-grained and dense in structure. It is possible to deposit gold coatings on brass in thicknesses of the order of 0.0001 inch which show no evidence of pinhole corrosion in the usual accelerated corrosion tests. Generally for contact surfaces, deposits of 0.0005 inch are recommended.[14] The use of nickel as an undercoating for gold has been recommended for the protection of steel.[15]

"Gold filled" articles, such as watch cases, are stamped from gold-plated sheet made by soldering a sheet of gold or gold alloy to a slab of nickel-silver or brass. The soldering is accomplished by inserting a thin sheet of "brazing" alloy between the gold and the basis metal. It is necessary to heat the material only above the melting point of the braze which is considerably lower than that of either the gold or the basis metal.

According to a decision, January 25, 1923, of the U. S. Federal Trade Commission relating to the gold-filled watch-case industry, the minimum thickness of the gold layer on such gold-filled plate must be 0.003 inch on the outside of the case and 0.001 inch on the inside.

By the use of proper reducing solutions gold and silver can be reduced to the metallic form from their solutions, and coatings obtained directly by this means. This method is used principally for the production of mirrors, however, rather than for coating other metals.

RHODIUM COATINGS

Rhodium may be electrodeposited as a bright pinkish-white coating which is not tarnished appreciably in the air and which is not dissolved even in hot aqua regia.[16] It has come into commercial use in the jewelry and reflector industries where tarnish resistance and high reflectivity are attractive attributes. In the manufacture of reflectors for searchlights rhodium is deposited on undercoatings of electrodeposited copper.[17] There is some doubt as to the suitability of rhodium coatings for the protection of silver tableware from tarnish. For one thing rhodium differs slightly from silver in appearance. While rhodium is somewhat harder than silver, it may be expected to be scratched and otherwise damaged by the usage to which tableware is subjected, with the result that the rhodium coating will be removed in places, permitting the underlying silver to tarnish and darken. It is reported that rhodium-plated silver contacts have been used successfully in telephone apparatus.[18]

Rhodium may be plated from a sulfate bath containing ammonium sulfate operating at about 50° C. (122° F.) and at current densities not to exceed 9 amperes per sq. dm. (0.6 ampere per sq. in.).[19] Very satisfactory deposits may be obtained also from a solution of ammonium rhodinitrite.[16]

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[13] Blum, W., and Hogaboom, G. B., "Principles of Electroplating and Electroforming," 2nd ed., New York, McGraw-Hill Book Co., 1930.

[14] Anon., *Oberflächentechnik*, 14, 2 (1937).

[15] Leonhardt, R., and Steel, P., *Oberflächentechnik*, 10, 83 (1933).

[16] Atkinson, R. H., and Raper, A. R., *Metal Ind. (London)*, 44, 191 (1934).

[17] Schwartz, M. W., *Metal Ind. (New York)*, 36, 14 (1938).

[18] Anon., *Funktech. Monat.*, No. 2, 68 (Feb., 1936).

Rhodium coatings are generally of the order of 0.00001 inch in thickness. Attempts to produce appreciably heavier coatings have not been successful.

PLATINUM AND PALLADIUM COATINGS

Platinum and palladium coatings have been used, like gold, to a limited extent for protective coatings and for electrical contacts. Platinum has been electroplated for many years, usually from a complex phosphate bath. More recently it has been shown that both platinum and palladium may be more satisfactorily deposited from amminonitrite solutions.[20] These baths are used at 90-95° C. (194-203° F.). The throwing power of the solutions is good enough to permit satisfactory covering of all recessed areas of jewelry parts. The coatings are bright and do not require buffing. A non-porous deposit of palladium requires a coating 0.0002 inch in thickness.[21] Coatings of the platinum metals, notably palladium, may be fabricated by mechanical methods. This may be accomplished by welding layers of the noble metal on nickel strip and rolling down to the desired dimensions.

INDIUM COATINGS

Indium is one of the rarer elements. It usually occurs in small amounts with certain zinc ores from which it is recovered by chemical and electrochemical methods.[22] Indium is a very soft, ductile metal of a gray, lustrous appearance. It melts at 115° C. The metal is now available in commercial quantities.[23]

Although indium was electrodeposited as long ago as 1904, it was only recently that a practical plating process was developed.[24] The plating bath is prepared by dissolving precipitated indium hydroxide in a concentrated sodium cyanide solution and adding 0.5 gram of glucose for each gram of indium present.[25] The bath is operated at room temperature at current densities from 1 to 16 amperes per square decimeter.

Indium electrodeposits are silver-white in color and of a satin-like texture. Indium remains bright in the air and is more resistant to tarnish than is silver. The coating is soft and may be scratched with the fingernail. As mentioned previously in the discussion of tarnish-resistant silver alloys, it is possible to electrodeposit alloys of indium with silver. These alloys are harder than either of the two metals alone.

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[19] Fink, C. G., and Lambros, G. C., *Trans. Electrochem. Soc.*, 63, 181 (1933).

[20] Keitel, W., and Zschiegner, H. E., *Trans. Electrochem. Soc.*, 59, 273 (1931).

[21] Atkinson, R. H., and Raper, A. R., *J. Electrodepositors' Tech. Soc. (London)*, 10, 1 (1933).

[22] Westbrook, L. R., *Trans. Am. Electrochem. Soc.*, 57, 289 (1930).

[23] Murray, W. S., *Ind. Eng. Chem.*, 24, 686 (1932).

[24] U. S. Patents 1,847,941 (March 1, 1932); 1,849,293 (March 15, 1932).

[25] Gray, D., *Trans. Electrochem. Soc.*, 65, 377 (1934).

RHENIUM COATINGS

Rhenium is a rare metal rather widely distributed in small amounts in certain molybdenum and platinum ores. It was discovered as recently as 1925, and named after the river Rhine. Rhenium has been successfully electrodeposited,[26] but so far as is known it has not been used commercially. It may be codeposited with cobalt and nickel. Rhenium coatings are mirror bright if plated on polished surfaces. Perhaps the most distinctive feature of rhenium coatings is a high resistance to hydrochloric acid solutions.

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[26] Fink, C. G., and Deren, P., *Trans. Electrochem. Soc.*, 66, 471 (1934).

Chapter 12

Methods of Testing Metallic Coatings

The serviceability of a metallic coating depends upon its quality in terms of continuity and uniformity, its physical and electrochemical relation to the basis metal, the character of the environment to which it is exposed, and the nature of the corrosion products which the coating metal forms in its chemical reactions with the constituents of that environment. Naturally, the best method of determining the protective value of a metallic coating is to employ it upon a trial basis under the conditions of actual service. Experience obtained in this way, although accumulated slowly and sometimes expensively, does contribute to the growing body of corrosion information and lends confidence in the selection of the coating for large-scale use. Ordinarily, helpful information concerning the performance to be expected of a metallic coating may be obtained from studies of the quality of the coating and from corrosion tests of some sort. The properties of importance in considering the quality of any metallic coating are: (a) the average thickness, (b) variations in uniformity of thickness, (c) porosity or continuity, (d) adherence to basis metal, (e) flexibility, and (f) presence and distribution of certain metallic impurities. Certain types of tests, to be described, may be made in a laboratory to furnish information upon these properties, and from this knowledge it is possible to infer a great deal concerning the protection likely to be provided by the coating.

Corrosion tests applied to metallic coatings are designed to determine how long a given weight or thickness of coating will preserve the basis metal in the performance of its intended function. When appearance is not an important factor, the endpoint of the test and likewise of the service life of the coating may not be defined sharply and may permit, as illustrated in Chapter 6, an appreciable degree of corrosion of the basis metal. Corrosion tests of coatings, as of metals in general, involve exposing the material to a more or less complex environment (such as the atmosphere, soils, water or chemical solutions), the non-metallic constituents of which react chemically with the metal. The progress of these reactions is determined and their endpoints observed either visually or by measuring changes in weight, in physical properties, in electrical resistance or electrode potential or by measurement of depth of pitting, etc.

DETERMINATION OF QUALITY OF METALLIC COATINGS

When the performance of a metallic coating in a given environment is known from experience, from corrosion tests or from general chemical knowledge, it becomes a relatively simple matter to control the quality of the product, and to predict its performance by means of physical or mechanical tests, for adherence and ductility of coating, and of certain chemical tests designed to determine coating thickness, distribution and continuity. The proportion of the product which it is necessary to test will, of course, depend upon the coating process and the standard of quality required. In general, coatings applied by mechanical methods ("metal-cladding"), and those applied by hot-dipping or electroplating to strip stock are likely to be more uniform and require less attention than those applied to individual parts of irregular shape. If, in addition to product requirements, the product is fabricated in accordance with a process specification, there is still further assurance that the coating will give the expected service life. Quality tests should be simple, rapid of application, and inexpensive. The information obtained from these tests may be qualitative in character, as for example that obtained concerning the degree of adhesion or brittleness, or local variations in thickness; it may be quantitative, as in the determination of the amount of coating or the number of pinholes per unit area of surface.

Tests for determination of ductility and adherence of coatings are made when these qualities are likely to have a bearing upon performance. These tests are physical in character, and are applied prior to tests of thickness and uniformity of the coating. Usually such tests are designed to subject the coated material to the type and extent of deformation to be experienced in service. On account of the commercial importance of zinc coatings on sheet and wire stock—materials likely to undergo deformation—the physical tests to be described will relate primarily to coatings of this kind. Tin, aluminum and lead coatings applied to sheets might be tested in a similar manner.

Physical Tests

Bend Test for Sheets.—Zinc-coated sheets are often tested by being bent double over a mandrel of specified diameter, which is usually expressed in terms of the thickness of sheet tested. In order to pass the test, the coating on the convex side of the bent sheet must show no signs of serious injury at the completion of the test. Even when carefully conducted, the bend test yields only qualitative results.[1]

It is often a matter of uncertainty as to what constitutes failure of the coating when a coated sheet is tested in this manner. In any series of tests, the results may range from minute cracks, readily visible only with a magnifying lens, at one extreme, to a pronounced flaking of the coating at the other extreme. Obviously, the criterion which should be used in determining what constitutes failure of the coating is the behavior of the bent specimen when subjected to corrosive conditions. It has been shown,[1] for example, by such corrosion tests that the serviceability of the coating with respect to severe corrosive conditions is not impaired unless the cracks in the bent coating are wide enough so that the basis metal beneath is clearly exposed.

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[1] Stacy, H. A., *Am. Inst. Mining Met. Eng., Preprint 1600C* (1926).

Bend tests of coated sheets are usually made in a simple manner by means of a vise. In using any such method, however, care must be taken to control the speed at which the specimens are bent since, as is shown in Figure 54, sheets which can be bent double without material damage to the coating if the bending is done slowly enough may flake very decidedly along the line of the bend if the operation is carried out very rapidly. This is more likely to be the case with zinc coatings having a large, well-developed spangle than with those having a small spangle. Experience has shown also that the temperature at which bend tests are made may affect the results. A temperature of 18° C. (65° F.) has been suggested as a minimum for specification use.[1]

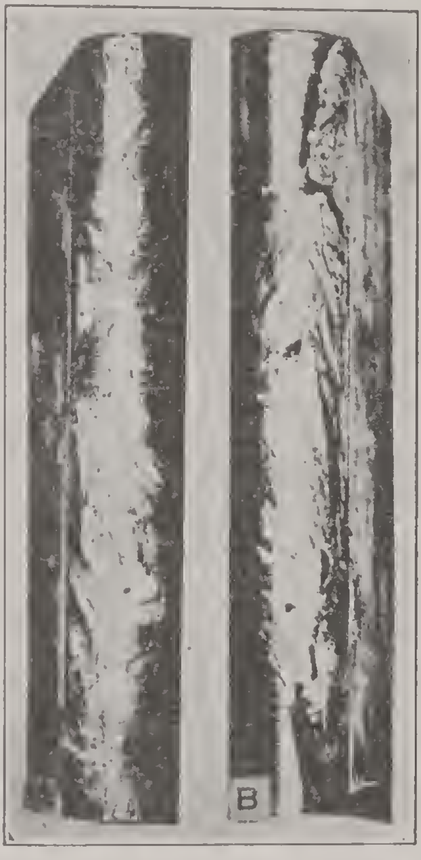

Figure 54.—Effect of Speed at Which the Bend is Made upon the Results of Bend Tests of Galvanized Sheet. ×1.[1]

The bend test, aside from a practical corrugation test, was not used formerly to any extent in American specifications for zinc-coated sheets, but it has come to be introduced as a requirement into certain specifications of coated sheet.

Other bend tests used for coated sheets are the 90-degree bend and "seaming" tests. These are essentially shop tests. Results obtained with the Erickson "cupping" test on coated sheets have shown that this test is not nearly so suitable for revealing the properties of the coating as is the more simple bend test.

Bend Test for Wire.—The bend test as applied to coated wire is carried out usually by wrapping the wire in the form of a close helix around a cylindrical mandrel. The coatings are graded according to the diameter of the mandrel around which the wire can be wrapped without failure of

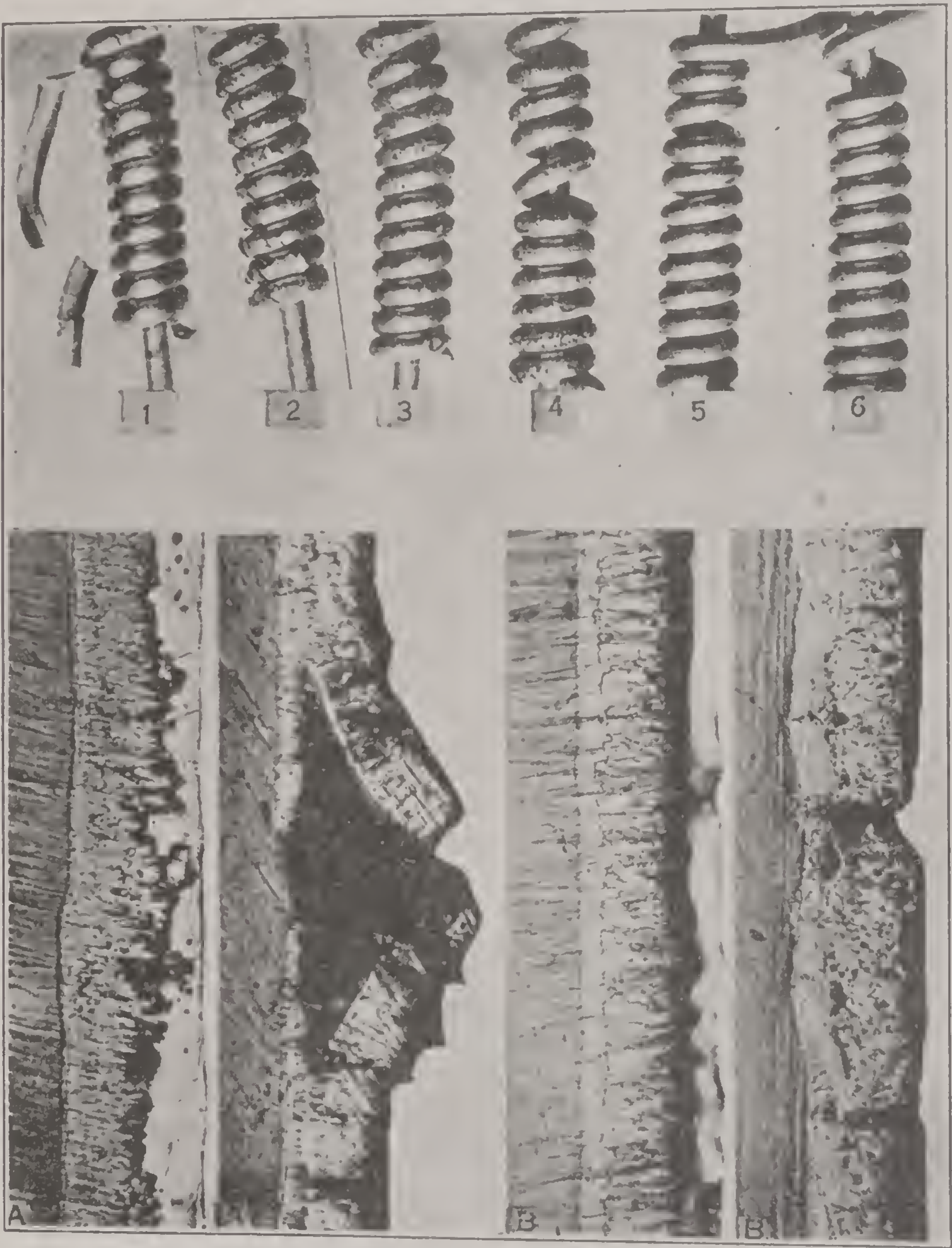

Figure 55.—Representative Bend Cuts of Galvanized Wires, No. 12 gauge.[27] The bending properties of wire are evidently influenced by the composition of the base. The coating on the wires of higher carbon content (Nos. 5 and 6) shows evidence of better adherence than on other wires.

the coating.[2] In practice, the most severe test of this kind is to wrap the coated wire closely around a wire of its own diameter as is shown in Figure 55.

[2] *Proc. Am. Soc. Testing Materials*, 26, pt. 1, 664 (1926).

Atmospheric exposure tests upon coated wire which has been bent and has developed cracks or fissures in the coating indicate that heavy coatings, even when brittle, offer greater protection to steel than do light coatings. When, however, particles of the coating flake off, exposing areas of bare iron of appreciable size, rusting occurs. It has been suggested[3] that more significant information concerning the role of brittleness might be obtained by determining the reduction of the corrosion or quality test-value of a coating produced by the application of a standard wrapping test.

Adhesion Tests.—No very practical test of a quantitative character for the adhesion of metallic coatings has ever been reported. Some years ago[4] it was proposed to solder a metal strip to a plated coating and then measure the force required to detach the coating. In addition to the difficulty that thin coatings offer to soldering it seems likely that their adherence will be affected by the soldering operation. Another method[5] of determining adhesion consists in measuring the force necessary to detach a plated coating from the end of a cylindrical rod. Although it is possible by these methods to measure large differences in adhesion on different bases, the results are not accurately reproducible.[6] Moreover, tests of this type are not suitable for the routine testing of coated metals.

The bend tests, previously described, furnish considerable information as to the adherence of coatings. However, probably the best assurance of satisfactory adhesion is to be obtained, not from measurements of the property by existing methods, but from the knowledge that the basis metal was properly prepared for coating and that the coating process was carefully controlled.

Tests for the Average Thickness of Coating

A variety of methods have been devised for determining the average thickness of coating. Some of these are capable of general application while others are restricted to certain coatings. Those methods most commonly used for zinc coatings are chemical stripping methods; for the determination of such coatings as silver and nickel, the coating is removed usually by electrolytic means. In most of these cases, the weight of coating is determined rather accurately by weighing on an analytical balance an article having a measured area of the coated surface, removing the coating and determining from the loss of weight the thickness or weight per unit area. Other methods of measurement of coating thickness make use of the heat developed, the gas evolved or the electrical current required in dissolving the coatings in an acid or other solution.

The weight of hot-dipped zinc coatings on sheets may be determined in the shop by weighing the pickled and washed sheet (after it has drained for 2 minutes), galvanizing and afterwards reweighing the sheet.[7] For coated sheets it is common commercial practice to express the weight of coating in terms of a unit of *sheet* rather than a unit of *surface*. A sheet bearing a 2-ounce zinc coating has 2 ounces of coating for each square foot of sheet, that is, one ounce per square foot on each side. In other cases, such as pipe, wire and hardware, the coating is expressed in terms of a unit area of surface.

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[3] Britton, S. C., *J. Inst. Metals*, 58, 211 (1936). This paper presents an excellent review of methods of test applicable to zinc coatings.

[4] Burgess, C. F., *Electrochem. and Met. Ind.*, 3, 17 (1905).

[5] Ollard, E. A., *Trans. Faraday Soc.*, 21, 81 (1925).

[6] Blum, W., *Monthly Rev. Am. Electroplaters' Soc.*, 23, 5, Nov. (1936).

Sampling of Zinc-coated Sheets and Wire.—Laboratory determination of the weight of coating on zinc-coated sheets is almost always carried out on square specimens 2.25 by 2.25 inches. The advantage of using this size is the fact that the weight of the coating in grams is numerically equal to the weight as expressed in ounces per square foot. In sampling sheets, the American Society for Testing Materials has recommended that a strip 2.5 inches wide be cut transversely or diagonally across the middle of the sheet with its ends approximately one inch from the edge of the sheet and that three specimens, cut accurately to size 2.25 by 2.25 inches be used, one from the middle and one from each end of the strip.

In sampling wires, 12-inch lengths are convenient specimens to use. It is more convenient in routine work to use such a length that the weight of coating in grams as determined in a stripping test will equal numerically the weight of coating as expressed in ounces per square foot of surface. Both the diameter and length of specimen must be taken into consideration. Table 28 gives the length to be used for wires of different diameters.

Table 28.—Sampling of Zinc-Coated Wire.*[7]

Birmingham Wire Gauge	Size of Wire Diam. (Inch)	Length of Wire for Test	
		Inch	Cm.
0	0.340	$4\frac{3}{4}$	12.1
1	.300	$5\frac{3}{8}$	13.7
2	.284	$5\frac{11}{16}$	14.5
3	.259	$6\frac{1}{4}$	15.9
4	.238	$6\frac{13}{16}$	17.3
5	.220	$7\frac{3}{8}$	18.7
6	.203	$7\frac{15}{16}$	20.2
7	.180	9	22.8
8	.165	$9\frac{13}{16}$	24.9
9	.148	$10\frac{15}{16}$	27.7
10	.134	$12\frac{1}{16}$	30.6
11	.120	$13\frac{1}{2}$	34.2
12	.109	$14\frac{13}{16}$	37.7
13	.095	17	43.2
14	.083	$19\frac{1}{2}$	49.5
15	.072	$22\frac{7}{16}$	57.0
16	.065	$24\frac{7}{8}$	63.2
17	.058	$27\frac{7}{8}$	70.8
18	.049	33	83.8

* The weight of coating in grams for the specimen is numerically equal to the weight of coating for the wire expressed in ounces per square foot.

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[7] *Am. Soc. Testing Materials Standards,* A90-24, 325 (1924).

For pipes, it is frequently desirable to determine separately the weight of coating of the outside and the inside surfaces. For miscellaneous hardware, a definite sampling procedure is not practicable on account of the diversified nature of such products. For small pieces, the entire article is used and in the case of nails, bolts, nuts, rivets and other fasteners several of the articles are combined as one sample, the number used depending upon the size in each case. Since cutting samples from sheet-metal ware, ash cans, garbage cans, tanks, laundry tubs and the like, as well as culverts, is not desirable, the "spot" test may often be found the most satisfactory method of testing such materials.

Hydrochloric Acid-Antimony Chloride Method.—This method, which was first described in 1915,[8] has been designated as standard by the American Society for Testing Materials for zinc and cadmium coatings.[9] It has been applied more recently in a rapid test for determining the thickness of tin coatings on steel.[10] The procedure consists in the removal of the coating from an accurately measured and weighed sample by immersion in concentrated hydrochloric acid (sp. gr. 1.19) to which has been added 5 cc. of antimony chloride to each 100 cc. of acid. The antimony chloride, prepared by dissolving 20 grams of antimony trioxide or 32 grams of antimony trichloride in one liter of concentrated hydrochloric acid, is used for the purpose of inhibiting the attack of the acid on the basis metal when the coating has been removed. Unless the test specimen is allowed to remain in the acid for several minutes after the evolution of hydrogen ceases, the attack on the basis metal is entirely negligible so far as the accuracy of results of this test for commercial purposes is concerned.

In the test procedure the specimen with a measured area is degreased with an organic solvent, rubbed lightly with magnesium oxide paste if necessary, and well rinsed. It is dried and weighed and then immersed in a suitable volume of the test solution until the evolution of hydrogen has practically ceased. This requires about 15 to 30 seconds, except in the case of sherardized coatings which require a somewhat longer time. The temperature of the solution should not exceed 38° C. (100° F.) during the test. After stripping, the specimen should be washed and scrubbed under running water, rinsed with alcohol, wiped dry, dried at 100° C. (212° F.), cooled and reweighed.

In stripping tin coatings from a steel base by this method, a thickness of 0.0001 inch of tin requires about 1 minute.[10] The tin-iron alloy layer in hot-dipped tin coatings is readily dissolved in the solution.

The method is applicable to testing zinc-coated wire, in which case a small piece of wire should be stripped of its coating by a preliminary test and the diameter measured on this rather than on the coated wire. If the length of wire given in Table 28 is used, the loss of weight in grams is equal to the weight of coating expressed in ounces per square foot of actual surface.

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[8] Aupperle, J. A., *Proc. Am. Soc. Testing Materials,* 15, II, 119 (1915); *Iron Age,* 96, 132 (1915) (Abstract).

[9] Committee A-5, *Proc. Am. Soc. Testing Materials,* 33, pt. 1, 140 (1933).

[10] Clarke, S. G., *Analyst,* 59, 525 (1934).

Sulfuric Acid-Arsenious Oxide Method.—This method for determination of the weight of zinc coatings produced by hot-dipping, and also for distinguishing between these coatings and those produced by electroplating, consists in the use of dilute sulfuric acid containing arsenic which serves as an inhibitor.[11] For general purposes, it has been found that a solution containing 100 cc. of concentrated sulfuric acid (sp. gr. 1.84) and 5 grams of arsenious oxide per liter has the advantage of being more rapid in action than that proposed originally.[12] Where a high degree of accuracy in the determination of weight of coating is unnecessary, the inhibitor may be omitted, as is the case in the standard specifications of the American Society for Testing Materials [9] which employs a solution of 40 cc. of concentrated sulfuric acid in 960 cc. of distilled water.

Hot-dipped coatings are distinguished from electroplated coatings in this process by the appearance in the solution at the end of the test of appreciable quantities of iron derived from the iron-zinc alloy layer. If lead has been used in the hot-dipping process, it shows in part as adhering spots on the test sample and also as flocks in the solution. For electroplated zinc, the solution is clear, free from iron and there is no evidence of lead.

Basic Lead Acetate Method.—This method of removing a zinc coating [13] has been recommended by the American Society for Testing Materials as an alternative method. A solution is prepared by dissolving 400 grams of crystallized lead acetate in 1 liter of distilled water and adding to this solution 4 grams of finely powdered litharge. The solution is allowed to settle and the clear portion used. After being degreased the specimens are immersed in an upright position in the solution for about 3 minutes; they are then removed and the adhering lead is brushed off under running water. Care must be taken not to burnish the lead onto the surface. Four 3-minute immersions are usually sufficient for complete removal of the coating, after which the stripped samples are dried and the loss of weight determined.

The lead acetate method depends upon the fact that lead is electropositive to zinc and is therefore displaced from solutions of its salts and deposited in the metallic form, usually as a loosely adherent precipitate on the bare iron areas of the test specimen. The method is similar in accuracy to the hydrochloric acid-antimony chloride method. It should not be used for coated articles of irregular shape, as the complete removal of the precipitated lead from crevices and re-entrant angles is not easily accomplished.

The difficulty in determining the true surface area of objects of irregular shape presents difficulties in most methods of test. In the case of zinc-coated nails, the weight of coating is reported in per cent of weight of the original coated nail.

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[11] Bauer, O., *Mitt. Material*, 32, 456 (1914).

[12] Kenworthy, L., *J. Inst. Metals*, 61, 143 (1937).

[13] Patrick, W. A., and Walker, W. H., *J. Ind. Eng. Chem.*, 3, 239 (1911).

Other Chemical Stripping Methods.—Many other methods of removal of coatings have been proposed. For zinc coatings, for example, solutions of acetic acid, phosphoric acid,[14] and alkali and alkaline earth bisulfates or bisulfites [15] have been described, but they do not appear to offer any advantage over the solutions mentioned in the foregoing sections.

For stripping tin from tinned copper wires a solution consisting of 100 grams of ferric alum in a liter of water to which is added 50 cc. of hydrochloric acid (sp. gr. 1.12) and 25 cc. of phosphoric acid (sp. gr. 1.7) has been recommended.[16]

In the removal of cadmium coatings a solution of ammonium nitrate containing 120 grams per liter is sometimes used. At 40° C. (104° F.) this solution dissolves about 0.001 inch of cadmium in 10 minutes. Still another solution for stripping cadmium deposits contains 50 grams per liter of ammonium persulfate and 100 cc. per liter of concentrated ammonium hydroxide.[17] In this test about 0.001 inch of cadmium is removed in an hour.

Electrolytic Methods.—As mentioned earlier, most metallic coatings are readily removed by anodic dissolution in suitable electrolytes. For zinc coatings, a 10-per cent solution of potassium cyanide has been proposed; [18] other solutions in which zinc is not highly polarized anodically may be used. The same considerations apply to other metals.

The thickness of the coating removed electrolytically is generally calculated from the loss in weight of the specimen or from a chemical analysis of the solution containing the dissolved metal. More recently an electrolytic test [3] for zinc coatings on wire has been developed which furnishes information as to the structure of the coating, as well as its thickness. In this test the procedure is to make the coated wire anodic at a constant current density in a cylindrical glass jar containing a solution of 20 parts of sodium chloride and 10 parts of zinc sulfate in 100 parts of water. A current density of 1 ampere per square inch (15.5 amperes per sq. dm.) is employed, which removes 0.104 ounce per square foot of coating per minute. Since the successful use of this method requires the application of a uniform current density to all parts of the coating being tested—a condition readily satisfied for wire and sheet—it is difficult to use in testing articles of irregular shape.

Information concerning the phase structure of metallic coatings may be obtained from observing the anodic potential of the coating and its change with time during the anodic dissolution of the coating.[19] Applied to zinc coatings,[3] the method, as illustrated in Figure 56, clearly distinguishes between hot-dipped and electrodeposited coatings. It is seen, as is well known, that the potential of the zinc-iron alloy layer is intermediate between the potentials of zinc and iron. Since the coating is removed at a uniform and known rate from the wire, the time required for dissolution corresponds to a definite weight or thickness of coating. Referring to the various sections of curve 1 of Figure 56, it will be observed that the portion AB represents the pure zinc part, CD the alloy layer, and AE represents the entire coating. Curves 2 and 3 are indicative of coatings which either possess very thin alloy layers or are so uneven that the iron base is bared in some areas before the coating is dissolved from others. Curve 4 shows to what extent coating thickness is reduced by close-wiping; curve 5 reveals the absence of the zinc-iron alloy layer in electrodeposited coatings; and curve 6 shows that substantially all of the coating becomes converted into the alloy phase by annealing—the so-called "galvannealed" coating developed a few years ago.[20]

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[14] Heise, G. W., and Clemente, A., *Philippine J. Sci.*, [A] **11**, (4) 135 (1916).

[15] Broemme, E., and Steinau, R., U. S. Patent 1,042,315 (1912).

[16] Schürmann, E., and Blumenthal, H., *Electrotech. Z.*, **48**, 1295 (1927).

[17] Blum, W., Strausser, P. W. C., and Brenner, A., *J. Research Bur. Standards*, **16**, 185 (1936).

[18] Korpiun, J., *Metallwaren-Ind. Galvano-Tech.*, **32**, (16) 364 (1934).

[19] Glazunov, A., *Trans. Faraday Soc.*, **31**, 1262 (1935).

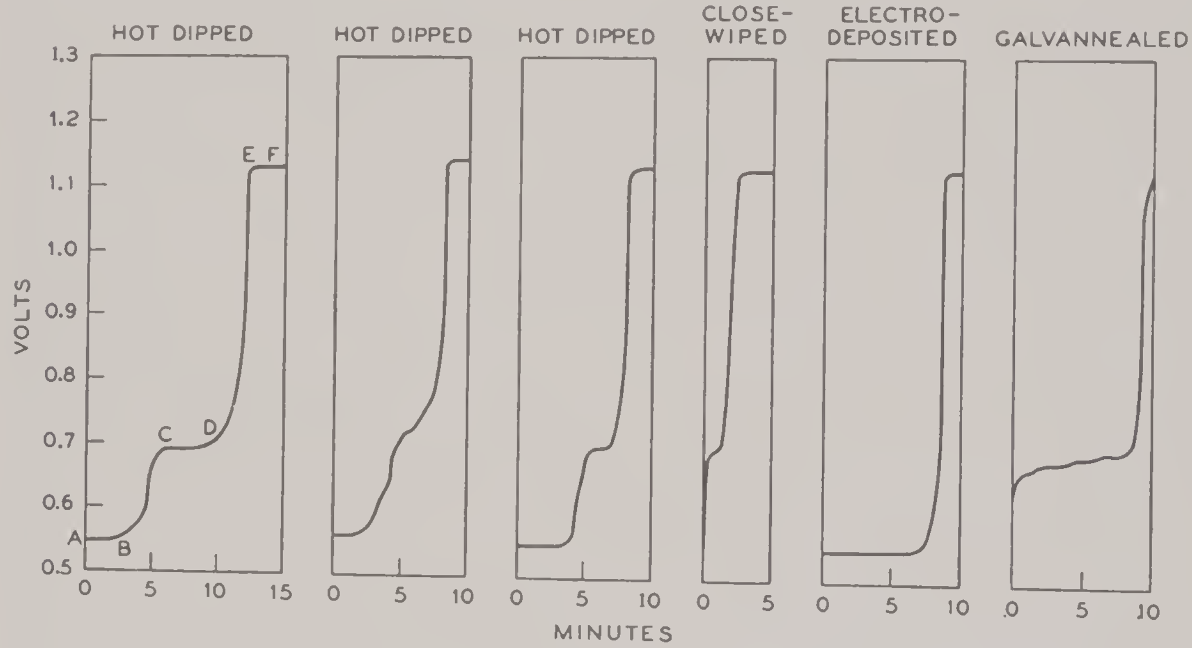

Figure 56.—The Change in Potential of Zinc Coatings during Anodic Dissolution of Coating.[3]

Hydrogen Evolution Method.—This method consists in measuring the quantity of hydrogen liberated upon dissolution of the coating in an acid.[21] While it may be carried out on small articles by immersing them in the solution, the usual procedure is to clamp an inverted cup on an area of the surface, introduce hydrochloric acid containing antimony chloride, and collect the hydrogen evolved in a burette attached to the cup. The composition and concentration of the stripping reagent may be those given previously in the description of the hydrochloric acid-antimony chloride method. The application of this test on different areas of the surface may be employed as a means of determining the distribution as well as the average weight of coating.

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[20] Schueler, J. L., *Trans. Am. Electrochem. Soc.*, **47**, 201 (1925), U. S. Patent 1,357,907.

[21] Cushman, A. S., *Proc. Am. Soc. Testing Materials*, **20**, (II), 411 (1920).

The weight of coating is readily calculated from volume of hydrogen obtained in the dissolution of a measured area of the coating; 1 cc. of hydrogen at 0° C. (32° F.) and normal atmospheric pressure (760 mm. of mercury) corresponds to 2.92 mg. of zinc.

Heat of Reaction Test.—A method has been described[22] for the evaluation of the weight of a zinc coating based upon the heat of the chemical reaction which occurs when it is dissolved in acid. The method is especially applicable to sheet and wire. The volume of solution, as well as the mass of the specimen immersed, must be controlled. The maximum rise of temperature attained by the solution is noted, and the weight of coating is calculated by means of a formula derived empirically by using a series of weighed and measured specimens of zinc-coated material of the same kind as the unknown material to be tested.

In the test procedure, 200 cc. of concentrated hydrochloric acid is poured into a jar of about twice this capacity. After stirring the acid and measuring its temperature to within 0.1° C., the measured coated specimen is immersed in the acid and the maximum temperature attained during the process is measured.

While the method has the advantage of simplicity and rapidity when once standardized, it is liable to serious errors. In the first place, the rise in temperature will depend upon the heat capacity of the system, and this may be markedly influenced by the mass of the specimen being tested, as well as the ambient temperature. Another factor which may affect the test is the markedly different heats of reaction of zinc and iron, which means that the result obtained will vary with the proportion of alloy in the coating.

Magnetic Methods of Test.—Magnetic methods of determining the thickness of coatings have been applied to coatings of non-magnetic metals on an iron base,[25] and to coatings of nickel, a magnetic metal, on a base of non-magnetic material such as brass.[26] The test procedure consists in measuring either the current necessary to detach a magnetized needle or the force necessary to pull an electromagnet or a permanent magnet from the coated surface. For the latter measurement, a simple spring balance is suitable.

In the case of non-magnetic coatings on steel the attractive force decreases less rapidly than a linear inverse function of the coating thickness, while in the case of nickel coatings on a non-magnetic base, the attractive force between the coating and the magnet is directly proportional to the thickness of coating. An accuracy of ± 15 per cent is claimed for both applications of the method.

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[22] Strickland, D. M., *Proc. Am. Soc. Testing Materials*, **22**, (II), 227 (1922).

[25] Radchenko, I. V., and Shestakovskii, F. K., *Zhurnal Tehnicheskoi Fiziki*, **5**, 1372 (1935); Brenner, A., *J. Research Bur. Standards*, **20**, 357 (1938). RP 1081.

[26] Brenner A.. *J. Research Bur. Standards*, **18**, 565 (1937).

The magnetic method has been shown to be suitable for the commercial testing of nickel-plated brass plumbing fixtures and a practical magnetic balance has been developed for this purpose.[26] The presence of chromium coatings of the usual thickness over the nickel does not interfere with the measurement. The test may be used to determine the uniformity, as well as the average thickness of coating.

Metallographic Examination of Coatings.—Probably the most direct method of investigating the thickness, distribution and structure of coatings is by the microexamination of metallographic cross-sections. The method, however, is laborious and requires skill in the technique of preparing the specimen; it is not well adapted to soft metals, such as zinc, cadmium and lead, which tend to smear even when a harder metal, such as nickel or copper, is deposited upon or clamped against the surface of the coating to be measured.

The specimen is prepared for examination by facing on a lathe after embedding in a soft metal such as zinc [27] or Rose's metal. More recently, substances such as Bakelite and the methacrylate resins have been found very satisfactory for fixing the specimen. The surface to be examined is polished successively with emery paper of increasing fineness down to that designated "0000," then with levigated alumina on the wheel, and finally with magnesia. After polishing, a suitable etching reagent is applied to bring out the structure into clear definition. For zinc coatings, a solution containing 20 grams of chromic acid and 1.5 grams of sodium sulfate in 100 cc. of water may be used.[27] Among other solutions proposed for this purpose are 1-per cent iodine in alcohol [28] or 3 per cent (by volume) of nitric acid in alcohol.[29]

In the measurement of thickness by this method a micrometer eyepiece is generally mounted on a standard microscope and a magnification of 100 to 500 diameters, depending upon coating thickness, is employed.

Tests for the Uniformity of Coatings

The protective quality of a metallic coating will often depend quite as much upon its uniformity as upon the level of its average thickness. Exposure of the basis metal in the areas of minimum thickness after a short period of use may greatly reduce the serviceability of the coating.

Preece Test.—The oldest and best known test for determining the uniformity and local thickness of zinc coatings is the "Preece" test, which consists in the gradual removal of the coating by repeated immersions in copper sulfate solution. The principle upon which the test is based is the displacement of copper ions from solution by the ions of zinc when this metal is immersed in a copper solution. Although the test has certain limitations (to be mentioned), it is widely used as a factory inspection or acceptance test for zinc-coated wires. It has been standardized abroad[30] and in this country[31] and recently an improvement in the method has been proposed[32] in tentative form for coated wire by the American Society for Testing Materials.

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[27] Finkeldey, W. H., *Proc. Am. Soc. Testing Materials*, 26, (II), 304 (1926).

[28] Rawdon, H. S., Grossman, M. A., and Finn, A. N., *Chem. Met. Eng.*, 20, 458, 530, 591 (1919).

[29] Heussner, C. E., *Monthly Rev. Am. Electroplaters' Soc.*, 23, 5 (1936).

The Preece test was proposed in 1857 by Dr. Max Pettenkofer[33] who suggested its use to the Bavarian Railway Commission for comparing the zinc coatings on telegraph wires from different sources. He suggested a 10-second immersion period in copper sulfate solution of 1 part in 12 parts of water. English wire was found to withstand 26 such immersions, whereas Bavarian wire failed in 16 dips. Later the test was used in England and the name by which it is generally known is that of Sir William Preece, who in 1884 strongly advocated its use for testing wire for the English telegraph lines.

The tentative standard method of the American Society for Testing Materials for coated wire is as follows. A copper sulfate solution is made by dissolving 36 parts by weight of commercial copper sulfate crystals in 100 parts by weight of distilled water; this solution is then shaken with an excess of powdered cupric hydroxide. The neutralized solution is filtered or is allowed to settle and then decanted, and it should now have a specific gravity of 1.186 (22.7° Baumé) at 18° C. (65° F.). The wire specimens selected are free from abrasion or cuts and are degreased before testing. A glass container at least 2 inches in diameter is filled to a depth of 4 inches or more for testing No. 12 gauge wire, and the same solution may be used for as many as 7 test specimens. The test specimens are placed in a fixed position in the copper sulfate solution for exactly 1 minute, removed, rinsed in water and wiped dry. The test solution is maintained at a temperature of 17 to 20° C. (62 to 68° F.) and the rinse water 15 to 21° C. (60-70° F.). Successive dips of 1 minute are continued until "the appearance of bright adherent copper indicates that the iron or steel beneath the coating has been exposed."

The test procedure described above may be applied to coated sheet and hardware, observing the same ratio of surface area to volume of solution which is given. Each one-minute immersion removes from 0.20 to 0.25 ounce of coating per square foot of actual surface. Tests on electroplated coatings have shown[17] that the endpoint is obtained for 0.001-inch coatings with approximately 4 one-minute dips.

The shortcomings of the Preece test have been investigated.[34] For example, it has been shown[35] that electroplated and sprayed zinc coatings dissolve more rapidly than do hot-dipped coatings. This difficulty may be overcome, of course, by specifying shorter periods of immersion for these coatings, but even this does not provide a very satisfactory basis of comparison of the two types of coating. Moreover, it is apparent that variation in the proportion of zinc-iron alloy in hot-dipped coatings will be reflected in a variable number of immersions required to give the endpoint.

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[30] British Standard Specification **No. 443** (1932).

[31] Test A90-33, *Book of A.S.T.M. Standards,* **1,** 317 (1933).

[32] Tentative Test A191-36T, *Proc. Am. Soc. Testing Materials,* **36,** pt. 1, 645 (1936).

[33] Pettenkofer, M., *Nat. Tech. Comm. München,* **1,** 159 (1857).

[34] Groesbeck, E. C., and Walkup, H. H., *Bur. Standards J. Research,* **12,** 785 (1934).

[35] Peirce, W. M., *Iron Age,* **114,** 199 (1924).

When relatively thin uniform electrodeposits of zinc are tested with the Preece test an endpoint of adherent copper may not appear, because the coating is so completely removed at one time that there remains no adjacent residual zinc to function as an anode with respect to the bare steel. This difficulty can be solved by attaching a piece of zinc gauze or screen to the test specimen.[17]

Still another difficulty with the Preece test is the occasional tendency to give premature endpoints, that is, the adherence of copper before the underlying steel is exposed. This behavior, which is more likely to occur with zinc coatings containing zinc-iron alloys, is believed [34] to be caused by the formation of plastic or colloidal material on the metal surface during the test; its effect may be eliminated by rubbing the specimen between immersions with a soft abrasive.

Acetic Acid-Hydrogen Peroxide Test.—Somewhat similar in character to the Preece test is the method of testing electrodeposited coatings for the appearance of rust in a solution of acetic acid containing hydrogen peroxide.[36] The solution consists of 140 cc. of 3-per cent hydrogen peroxide and 20 grams of acetic acid in one liter of water. The test is carried out at 95° C. (203° F.). The time in seconds required for the appearance of red-dust spots is noted. It is stated that the method is useful for showing the relative value of different zinc-plating processes, especially baths of different composition, although it is now known [12] that coatings prepared from cyanide baths dissolve at a slower rate than those deposited from sulfate baths. It does not seem to be suited to coatings containing a considerable proportion of iron.

Sulfuric Acid Test.—A specification test has been proposed for zinc coatings on wire in which the test specimen is immersed for a certain time in sulfuric acid containing arsenious oxide.[37] Following immersion in this test solution, the specimen is dipped in a concentrated ammonum sulfide solution, in which solution black spots are produced at points where the coating has been removed.

A somewhat analogous test [16] designed to reveal areas of minimum thickness in tin coatings on copper wire consists in dipping the coated specimen in hydrochloric acid, rinsing with water and then dipping in sodium polysulfide for the appearance of spots of black copper sulfide.

Dropping Tests.—The rate of solution of zinc or cadmium coatings has been found to be more constant if the solution is applied to the coating in successive drops instead of all at once as it is in immersion.[17] The method consists in allowing a given solution to drop at a uniform rate on a coated article mounted at an angle of 45° such that the solution, after striking the area under test, quickly runs off. The solution was first proposed for zinc coatings. The number of drops at a dropping rate of one drop per second required to perforate the coating gives, when calibrated, a direct measure of coating thickness. In the original method,[38] proposed for determining the local thickness of cadmium coatings, the solution recommended was one containing 100 grams of iodine and 200 grams of potassium iodide per liter of water. It is found that under the conditions of test 18 drops of solution was required for the dissolution of 0.0001 inch of cadmium and 22 drops for the same thickness of zinc. Later investigators [39] have substituted an acidified ammonium nitrate solution (100 grams of the salt and 55 cc. concentrated nitric acid per liter) for iodine and have increased the dropping rate to 90 to 110 drops per minute. Under these conditions, the rate of solution becomes nearly independent of the rate of dropping, making it possible to express the results merely in terms of the time of dissolution of coating. The test is carried out at 20 to 30° C. (70-90° F.). This modification of the test solution was designed for electroplated zinc coatings. For hot-dipped zinc coatings it has been found [17] that a satisfactory solution may be had by substituting 75 cc. of hydrochloric acid (sp. gr. 1.180) for the nitric acid proposed above. Similarly, a suitable solution for cadmium consists of 110 grams of ammonium nitrate and 10 cc. of hydrochloric acid per liter.

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[36] Wernlund, C. J., *Met. Ind. (New York)*, 23, 13 (1925).

[37] Drakonova, Z., *Zvetnye Metally*, 9, (4), 550 (1932).

Jet Test for Nickel and Other Coatings.—Somewhat similar to the dropping test is the jet test [40] for determining the local thickness of coatings. In this test, a stream of reagent from a small jet (the orifice of which in the test is capable of delivering 10 cc. of water in 30 seconds) is allowed to impinge on the surface in place of successive drops and the time required for penetration of the coating is observed. Otherwise the apparatus and method of arranging the test specimen resembles that employed in the dropping test. The rate of perforation is greater by a stream than with drops, making possible rapid testing of nickel and other resistant coatings. The test is non-destructive to the basis article which may be stripped and recoated.

For nickel coatings on steel, copper, brass, aluminum and zinc alloys, the solution adopted consists of 150 grams of ferric chloride ($FeCl_3 \cdot 6H_2O$), 100 grams of copper sulfate crystals, and 250 cc. of glacial acetic acid per liter.* Of this solution, the ferric chloride is the principal solvent. The copper present produces a coppered spot on certain of the basis metals at the point of perforation, while the function of acetic acid is to prevent localized attack at pores in nickel coatings on anodic basis metals like steel.

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[38] Clarke, S. G., *J. Electrodepositors' Tech. Soc.*, 8, No. 11 (1933).

[39] Hull, R. O., and Strausser, P. W. C., *Monthly Rev. Am. Electroplaters' Soc.*, 22, 9 (1935).

[40] Clarke, S. G., *J. Electrodepositors' Tech. Soc.*, 12, 1 (1937).

* This solution was later modified by Clarke. See *J. Electrodepositors' Tech Soc.*, 12, 157 (1937).

This solution operated at 22° C. (72° F.) penetrates 0.00001 inch of nickel per second. While this method can be used for copper coatings on various metals, a more suitable corroding solution for copper and bronze on steel consists in substituting, in the formula given above, 20 grams of antimony trioxide and 200 cc. of hydrochloric acid (sp. gr. 1.16) for the copper sulfate.

For zinc coatings on steel, the solution employed consists of 70 grams of ammonium nitrate and 8.1 cc. of hydrochloric acid (sp. gr. 1.16). This solution penetrates about 0.00002 inch of zinc per second.

Chord Method.—This method[23] for testing the thickness of metallic coatings consists in cutting through the coating on a curved surface with a flat file or on a plane surface with a precision grinding wheel of known radius. The thickness of coating, T, may be computed from the relationship, $T=C^2/8R$, where C (measured with a lens and scale) is the width of the chord, and R the radius of the curved surface or the grinding wheel.

This method is not applicable to coatings less than 0.0002 inch in thickness, but for heavier coatings including zinc and cadmium on steel it is said to be accurate within about 10 per cent. Some difficulty with smearing has been reported in the application of this method to soft coatings such as zinc.[24]

Other Tests for Uniformity of Coating.—As has been pointed out, electrolytic stripping tests if properly carried out dissolve the coating uniformly. It is obvious that under these circumstances the areas of minimum thickness will be revealed if the test specimen is inspected during the progress of the test.

Determination of Porosity.—The foregoing tests are designed to measure local variations in thickness of coating, such as often occur, particularly on irregularly shaped articles and where there are defects and pits not extending through the coating. In contrast to the purpose of these tests there will now be described a number of tests for the detection of pores and other flaws which extend through the coating and expose the bare basis metal.

"Ferroxyl" Test.—This test for revealing discontinuities, such as pinholes in tin coatings, was suggested in 1909 by Walker.[41] It is especially useful for coatings which protect the basis metal in a mechanical way. The usefulness of any such coating necessarily depends on its imperviousness; at any perforation the corrosive attack of the base metal, as a general rule, is accelerated by the "cathodic" coating. The test is applicable to tin and nickel coatings, but not to zinc coatings unless modified as described later.

In this test a solution of agar or gelatin in hot water, to which a small percentage of potassium ferricyanide and hydrochloric acid or sodium chloride has been added, is poured over a clean surface of the sheet of tin-plate to be tested, which is then allowed to stand for several hours, until the gel has solidified. Ferrous chloride formed by the action of the acid upon any exposed iron of the base metal reacts with the potassium ferricyanide to give a blue precipitate, Turnbull's blue, and thus marks (in the solidified gelatin film) the location of the pinholes in the coating. The solution for this test sometimes referred to as the "ferroxyl" test, may be prepared as follows: agar 1.0 gm., sodium chloride 10 gm., potassium ferricyanide 1 gm., and water sufficient to make 1 liter of solution. A few drops of phenolphthalein are added to the solution.

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[23] Mesle, F. C., *Met. Ind. (New York)*, 33, 283 (1935); Blum, W., and Brenner, A., *J. Research Bur. Standards*, 16, 171 (1936).

[24] Britton, S. C., Correspondence, *J. Inst. Metals*, 61, 164 (1937).

[41] Walker, W. H., *J. Ind. Eng. Chem.*, 1, 295 (1909).

The number and size of such spots vary considerably in different grades of tin-plate as shown in Figure 57. It has been questioned, however, whether each blue spot produced by this test necessarily indicates an opening in the tin coating, as the crystals of the iron-tin compound in the coating, which result from the alloying action of the molten tin on the iron in the hot-dipping process, will produce the same result, and thus erroneous conclusions as to the number of pinholes may be drawn.[42]

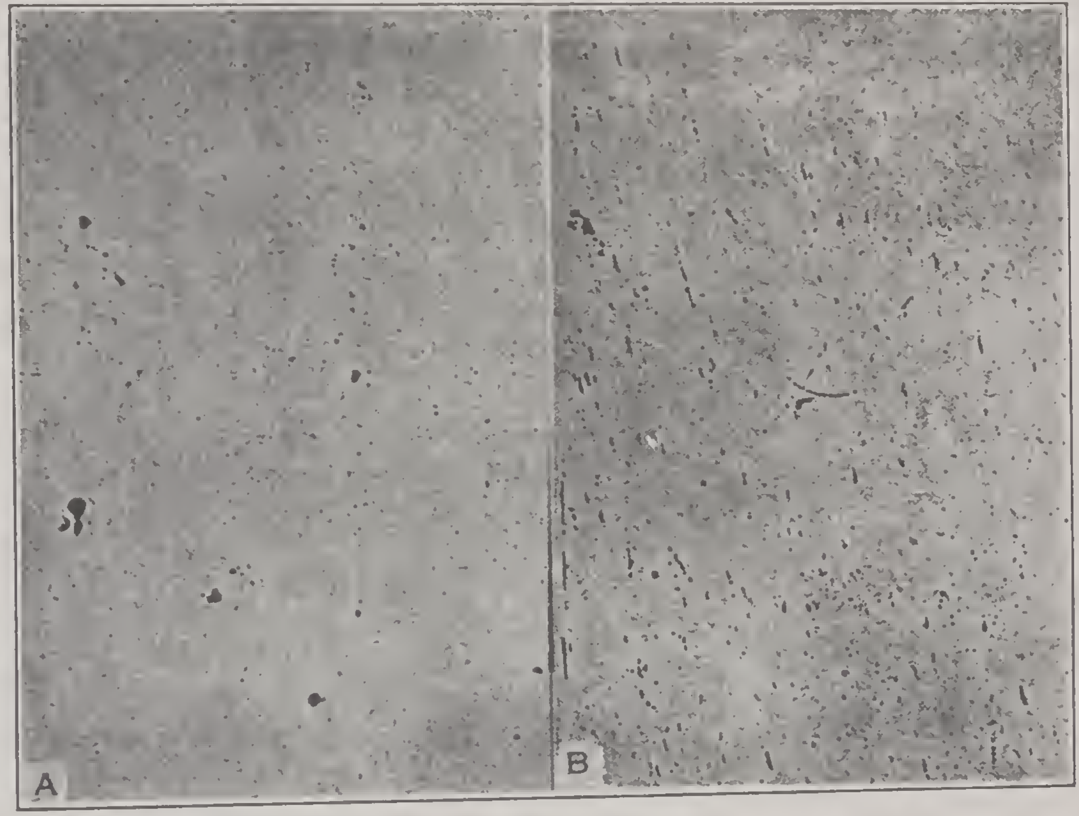

Figure 57.—Results of "Gelatin Test" on Tin-Plate.[42]

A. Commercial Charcoal Plate.
B. Commercial Coke Plate.
Each dark spot appears as a blue coloration in the gelatin film and marks the location of a "pinhole" perforation in the coating or perhaps in a few cases a crystal of iron-tin compound $FeSn_2$.

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[42] *National Canner's Assoc. Research Lab. Bull. 22L* (1923).

The ferroxyl test, in modified form, has been used with success in the study of the relative porosity of electroplated nickel coatings made under different conditions of deposition.[43] The solution for this purpose consists of 15 grams of agar, 6 grams of potassium ferricyanide, 60 grams of sodium chloride, 250 cc. of alcohol and 1 liter of distilled water, and is applied at 49° C. (120° F.). The pinholes which may be detected within 2 minutes are taken as a measure of quality.

In another modification of this test,[44] paper is impregnated with the reagents usually employed in the colloidal solution, and the treated paper, after being moistened, is held in contact with the coating which is to be tested for porosity.

More recently, paper impregnated with the reagent containing a lower concentration of potassium ferricyanide (0.5 gram per liter) has been employed satisfactorily in testing nickel coatings.[45] This technique may be used for nickel coatings containing deposits of copper or surface layers of chromium.

Zinc and cadmium coatings are anodic toward iron and cannot be tested by the ordinary ferroxyl test, since the exposed areas of iron thus cathodically protected do not provide the solution with the ferrous ions necessary for the formation of Turnbull's blue precipitate. If, however, an external e. m. f. is applied, of sufficient magnitude to overcome the protective couple action and send ferrous ions into solution at the pores in the coating, the method may be used for zinc and cadmium coatings. The more general application of this principle will be mentioned later in describing electrographic methods. In this modification of the ferroxyl test for application to zinc coatings [46] the reagent may be incorporated in gelatin or agar-agar and applied to the test specimen which is connected to the positive pole of a battery, or it may be applied by means of sensitized paper. The test may be carried out also in a liquid cell employing a 4-volt storage battery, a platinum cathode, and a solution consisting of 20 grams of potassium ferrocyanide and 1 gram of magnesium sulfate in 500 cc. of water.[47]

The same principle has been employed recently in the development of a porosity test for gold and other noble metal coatings on nickel.[48] The reagent consists of 3 grams of agar and 6 grams of sodium chloride dissolved in 100 cc. of water, made slightly ammoniacal with ammonium hydroxide; to this solution are added 10 cc. of a half-saturated alcoholic solution of dimethylglyoxime. The coated article to be tested, connected to the positive pole of a 6-volt storage cell, is placed in a small dish and covered with the warm reagent which is then allowed to gel. A layer of saturated sodium chloride solution is poured over the gel and a platinum wire cathode immersed in the solution. Employing a current density of 5 to 10 milliamperes per square centimeter, small red spots will appear in 2 to 5 seconds at all points where nickel is exposed.

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[43] Thomas, C. T., and Blum, W., *Trans. Am. Electrochem. Soc.*, **48**, 69 (1925).
[44] Pitschner, K., *Proc. Am. Soc. Testing Materials*, **27**, pt. 2, 304 (1927).
[45] Strausser, P. W. C., Brenner, A., and Blum, W., *Bur. Standards J. Research*, **13**, 519 (1934).
[46] Koehler, W. A., and Burford, R. O., *Trans. Electrochem. Soc.*, **70**, 397 (1936).
[47] Garre, G., *Arch. Eisenhüttenwesen*, **9**, 91 (1935).
[48] Test developed by C. H. Sample, Bell Telephone Laboratories, Inc., New York, Aug., 1937.

The Hot Water Test.—It has been found that a suitable method for revealing the porosity of tin coatings on steel consists in immersing the specimens, carefully degreased, in distilled water at 90 to 95° C. (194 to 203° F.) for 6 hours and observing the appearance of rust spots.[49] More recently, this test has been successfully applied to electrodeposited nickel coatings on steel.[50] Measurements of potential made in this connection show that nickel is cathodic to iron in distilled water at all temperatures from 20 to 100° C.

Sodium Chloride-Hydrogen Peroxide Test.—A somewhat similar test for the porosity of nickel, tin or chromium coatings on steel consists in immersion of the plated parts for about 4 hours in a dilute sodium chloride solution containing a small percentage of hydrogen peroxide.[51] The solution is prepared by adding 5.8 grams of sodium chloride and 3 cc. of 3.6-per cent solution of hydrogen peroxide to a liter of water. The larger pinholes appear within 30 minutes.

Electrographic Methods

Reference was made on a previous page to the detection of porosity by contact of the metal surface with sensitized paper. It was also pointed out that pores in zinc and cadmium coatings may be revealed by the application of an external e. m. f. of sufficient magnitude to overcome the protective couple action and send ferrous ions into solution. This principle is of general application for the detection of pinholes in all metal coatings (and even paint coatings) on any basis metal. It is a useful method also for the study of the nature and distribution of metallic impurities in a metal surface, and this will be mentioned later.[52]

The procedure in brief consists in employing the coated metal as the anode in a cell in which a smooth plate of aluminum or stainless steel is the cathode; a piece of filter paper moistened with a suitable solution serves as the intervening electrolyte. This cell is clamped together and a uniform pressure of the order of 100 pounds per square inch is applied. This pressure is required to insure complete contact of paper and metal surface, and to prevent lateral diffusion in the paper. The most suitable paper for the purpose is a thin hardened filter paper of fine texture. This must be backed up by a thicker loose-textured paper, which serves as a reservoir of electrolyte and provides a cushion which makes possible intimate contact of the printing surface and the specimen. An electrolyte suitable for most purposes consists of a solution containing about 5 per cent sodium carbonate and 1 per cent sodium chloride. The excess solution is removed beforehand by blotting and the paper rolled onto the surface in such a manner as to eliminate air bubbles. Sufficient potential is applied to the cell to overcome couple action between the coating and exposed basis metal, and the current permitted to flow for about 15 seconds. The paper member of the cell sandwich is then removed and immersed in a solution containing an anion, which with the cations of the basis metal will precipitate an identifiable compound of low solubility at areas in the paper corresponding to the location of the pinholes in the coating. In certain cases the procedure is simplified by having the precipitating reagent in the paper in the cell. For nickel coatings on steel a suitable impregnant is potassium ferrocyanide, and for tin-coated brass, a reagent paper containing precipitated antimony sulfide may be used, which is immersed in dilute phosphoric acid before use. In the first case, the pinholes are revealed by the appearance of spots of Turnbull's blue, and in the second case by the precipitation of copper sulfide.

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[49] Macnaughton, D. J., Clarke, S. G., and Prytherch, J. C., *J. Iron Steel Inst.*, 1, 159 (1932); *Intern. Tin Research Development Council Tech. Pub.*, Series A, No. 7, (1935).

[50] Hothersall, A. W., and Hammond, R. A. F., *Trans. Electrochem. Soc.*, 73, 449 (1938).

[51] Burns, R. M., *Discussion, Trans. Am. Electrochem. Soc.*, 52, 284 (1927).

[52] Jirkovsky, R., *Mikrochemie*, 15, 331 (1934).

Other Porosity Tests.—A test has been proposed[47] for the porosity of zinc and other coatings anodic to steel in which a visible cathodic product is produced. The test is carried out by immersing the coated specimen in a very dilute (0.001 to 0.004N) solution of potassium permanganate which upon cathodic reduction at the bare iron areas produces the black coloration of manganese dioxide.

The use of a boiling solution of sodium hydroxide for revealing the pinholes in zinc coatings was proposed some years ago.[41] In this test the location of any discontinuities in the coating by which the iron is exposed is shown by a stream of tiny bubbles of hydrogen at such points.

The porosity of gold coatings on brass may be strikingly detected by the exposure of the gold-plated parts to an enclosed mixture of air and nitric acid vapor at room temperature for several hours. Discontinuities in the coatings are revealed by fine "whisker-like" protrusions of blue corrosion products which develop at the site of the pores.[52a]

The salt spray test, to be described later, is sometimes employed to test the porosity of coatings. If continued for about 100 hours it yields results comparable to the more rapid ferroxyl test but has no advantage over this test for determining porosity.[45]

DETERMINATION OF RATE OF CORROSION

Essentially the determination of rate of corrosion consists in measuring the rate of a chemical reaction. In many of the environments in which metals are used more than one chemical reaction between a metal and the non-metallic constituents present may take place, either simultaneously or in succession. The usual corrosion test provides for the measurement, in some fashion, of the slowest of the chemical reactions involved in the process since it is the speed of this reaction which actually determines the rate of corrosion. Very often in ordinary corrosion tests the nature and identity of the chemical reaction which controls the process is not known.

[52a] Test developed by Mr. C. H. Sample of the Bell Telephone Laboratories, Inc., New York, N. Y. (1937).

The simplest corrosion test of a protective coating consists in exposing an article or specimen with a known thickness or weight of coating to a given environment and observing the period of time during which the coating provides satisfactory protection. The principal difficulty in the procedure is the variability of the environment, which may markedly affect the results. Recognition of this fact has led to a study of the various environmental factors which influence corrosion rates, and to attempts to control these and to standardize corrosion testing procedures.

Corrosion tests may be carried out in the laboratory or in the field under the conditions which are met in service. It is usually possible to exercise greater control in laboratory tests than in field exposures and consequently most studies having to do with the mechanism of the process and the influence of various factors on rate of corrosion have been carried on in laboratories. As a matter of fact, laboratory and field tests supplement each other; laboratory studies are helpful in explaining the results which occur in the field.

The problem of standardizing corrosion tests has lately received considerable attention.[53] Obviously, it is desirable to have available for specification purposes tests which can be depended upon to give reliable comparisons of the corrodibility of metallic materials. The full accomplishment of this goal requires a rather complete knowledge both of the environments in which metals are used and of the mechanisms of the corrosion reactions which take place. Practical experience and extensive experimental studies have contributed to these ends, and it would appear that certain tests are now ready for standardization. These include [53] field corrosion tests involving exposure to the atmosphere, soils and liquids and laboratory tests for determining resistance to impingement and intercrystalline attack, corrosion-fatigue, salt spray, partial immersion, and soil corrosion.

There are many pitfalls for those unfamiliar with the chemistry of metals who undertake to make corrosion tests. Among fallacies formerly prevalent, and at present not always detected by those who perform corrosion tests, was the idea that the rate of dissolution of any metal in an acid or other solution may be used to predict the life of the metal in the atmosphere or in another environment totally unlike the test solution. Then there is the failure to distinguish between quality and quantity of corrosion data —the belief that a great deal of data will in all cases lead to a conclusion which will be dependable.

Statistical methods for the analysis of corrosion test data have been used to a surprisingly limited extent. Recently, however, it has been shown that relatively simple standard statistical methods can be used to considerable advantage in the interpretation of corrosion results.[53] It should be emphasized, however, that the methods do not apply unless the data chosen represent a "random" sample.[54] Tests should also be made to insure that the distribution of the data follows the normal law of error, since the methods generally employed are based on the assumption of a normal distribution.

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[53] Borgmann, C. W., and Mears, R. B., *Symp. on Corrosion Testing Procedures, Am. Soc. Testing Materials*, p. 3, (1937).

Results of extensive tests of a qualitative or semi-quantitative nature, carried out in a variable environment, such as a natural atmosphere, lend themselves very well to statistical analysis. By suitable grouping and construction of frequency tables based upon observation of factors, such as amount of pitting and type of film, together with observations on variables, such as temperature, humidity and dustiness of air, quantitative correlation may be established between the different factors which can be made the basis of intensive quantitative tests. Similarly, the effect of factors suspected of influencing the results of quantitative tests may be determined by the application of tests for significance of differences in the mean values of results grouped so as to bring out the effect of the variable in question. The time and expense involved make it seldom possible to carry out accurate and carefully controlled tests in as large a variety of environments as would be desirable. By the use of statistical methods, the accurate control of environmental variables is sacrificed for results which are applicable to a much wider range of environmental conditions.[55]

It has been shown [56] that statistical methods can be used to separate the effect of constant experimental errors from the effect of variations in the material. It was thus possible to predict where further refinement in experimental technique would be justified. In some cases it is possible by an analysis of the data of a large number of observers for a given technique, or by conducting preliminary short time tests, to make a fair estimate of the probable error to be expected. If the maximum probable error desired is known, it is then possible to calculate for a contemplated set of tests the minimum number of identical specimens which should be used.

Atmospheric Corrosion Testing

Atmospheric corrosion tests of metallic coatings are for the most part conducted out-of-doors. Laboratory and indoor atmospheric tests are made in connection with tarnish studies where information is desired as to the appearance and probable life of noble metal coatings on such articles as jewelry or electrical contacts. The natural indoor air, for example, is representative of that in which such coatings are used and is measurably corrosive toward them in most cases. Laboratory tests employing synthetic atmospheres permit the production of tarnish films under controlled conditions and a study of the reactions involved. The progress of tarnish may be followed by gain in weight, change in electrical contact resistance, or by consumption of gaseous reactants. From the metallic coating standpoint, it is of interest to know the minimum thickness of coating required for a reasonable period of performance.

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[54] Fry, T. C., "Probability and its Engineering Uses," New York, D. Van Nostrand Co., Inc., 1928.

[55] Fisher, R. A., Statistical Methods for Research Workers, 6th ed., Oliver and Boyd, Edinburgh and London (1936); Shewhart, W. A., "Economic Control of Quality of Manufactured Product," New York, D. Van Nostrand Co., Inc., 1931.

[56] Mears, R. B., and Daniels, H. E., *Trans. Electrochem. Soc.*, 68, 375 (1935).

Laboratory atmospheric corrosion tests are sometimes carried out in rooms maintained at high relative humidity and an elevated temperature such as, for example, 95 per cent relative humidity and 95° C.; or a cycle of high and low humidities and temperatures may be employed. While these tests simulate the rather extreme climatic conditions prevailing in the tropics and at times in the southern Gulf coast in this country, they may be regarded as a type of "accelerated" test in comparison with the average atmosphere in which metallic materials are used. The performance of protective coatings in tests of this kind furnishes a certain amount of guidance in the selection of suitable finishes for tropical use.

Corrosion testing by exposure to outdoor atmospheres has become very general in the past 15 to 20 years. The most extensive tests are those which have been sponsored by the American Society for Testing Materials, the Atmospheric Corrosion Committee of the British Non-Ferrous Metal Research Association, and more recently, by the Corrosion Committee of the British Iron and Steel Institute and other similar organizations abroad. The National Bureau of Standards has carried on alone and in coöperation with technical societies a number of projects of this kind. In addition to these, many engineering and industrial concerns carry on more or less comprehensive field tests of metals and coatings in which they are interested.

A wide variety of atmospheric conditions have been provided in the sites selected for these tests. These include natural climatic factors, such as temperature, humidity and rainfall, and local contamination by dust, smoke, industrial gases, and salt from the ocean. In other words, test stations are established in rural, urban, industrial, marine, arid and moist regions. In some instances, attempts are being made to obtain information on atmospheric pollution and weather conditions at various test sites, and to correlate this with the corrosion results. There is considerable need for more detailed information as to the identities and concentrations of the constituents of the atmosphere which are destructive and those which are protective toward metallic materials before an intelligent rating of the corrosiveness of atmospheres can be made.[57] The amount of atmospheric pollution in an industrial area, such as New York City, is astonishing. Weather Bureau observations made in Central Park show that from 1.25 to 3 tons of dust are obtained daily per square mile of area from one cubic mile of air, and it has been calculated[57] from figures on the consumption of coal that more than a thousand tons of sulfur dioxide is released to the New York City atmosphere daily.

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[57] Finkeldey, W. H., *Discussion, Symp. on Corrosion Testing, Am. Soc. Testing Materials*, p. 52, (1937).

The specimens used in field tests are usually large in size and the area-weight ratio is made large[58] particularly where quantitative data on change in weight are sought. For example, the galvanized sheets employed by the American Society for Testing Materials were full-sized sheets (108 by 28 inches) from which two 30-inch sections representing the top and bottom were cut. The British Iron and Steel Institute employed a standard sample size of 10 by 15 by $\frac{3}{8}$ inches. A convenient size for electroplated specimens is 4 by 6 inches. Where change in tensile properties is employed to measure rate of corrosion, as in the testing of "Alclad" Duralumin, standard laboratory test specimens, or sheets from which such specimens may be cut, are employed. For studying the galvanic couple action of dissimilar metals in contact—a significant type of test from the standpoint of metallic coatings—a suitable test specimen consists of discs of the two metals clamped together but insulated from the clamping bolt and nut. Where the rate of corrosion is determined by means of the change in electrical resistance wire specimens of suitable size and length are employed.

The test specimens are generally mounted on strong racks in direct contact with grooved porcelain insulators which are bolted to the rack structures. It is customary to arrange sheet samples in an east-west line and orient them at an angle of 30 to 45 degrees to the horizontal facing south.

Inspections of field tests are made at intervals, the frequency of which depends upon the nature of the coated specimens and the rate of corrosion. Usually these examinations are made annually or semi-annually, and, in the case of tests sponsored by technical societies, by a committee which visits the various test sites in a body. A visual rating of specimens is made in the field, but where change in weight or tensile properties are to be determined it becomes necessary to send the specimens into the laboratory, where the usual methods of measurement are used. The depth of pitting may be determined either in the field or laboratory. Sufficient information for engineering purposes concerning the quality and performance of protective coatings can usually be obtained from visual observation of the field test results.

A convenient method of studying the corrodibility of metallic materials in the atmosphere (and in corrosive vapors)[59] is based on the principle that the resistance of a uniform conductor varies inversely as the area of its metallic cross-section. Specimens in the form of wire are mounted on suitable insulators and exposed to the corrosive medium. As corrosion progresses, the resistance of the specimens increases. The method has been employed with considerable success, and the results obtained have been shown to be in good agreement with those obtained by changes in weight and physical properties.[60] Among the advantages of the method are sensitivity, rapidity and the fact that it is unnecessary to remove the corrosion products in making a measurement.

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[58] Rawdon, H. S., *Symp. on Corrosion Testing Procedures, Am. Soc. Testing Materials*, p. 36 (1937). This paper contains an excellent review of atmospheric corrosion testing procedures, and has been used freely in the preparation of the present discussion.

[59] Burns, R. M., and Campbell, W. E., *Trans. Am. Electrochem. Soc.*, 55, 271 (1929).

Corrosion Testing in Liquids

Corrosion tests employing total immersion in liquid media are useful in furnishing information as to the extent of protection afforded by coatings against attack in those liquids and in providing an insight into the mechanism of the protective action. Immersion tests may be carried out under actual service conditions, or in the laboratory where the factors affecting rate of corrosion are readily controllable.

Field tests of metallic coatings under natural submerged conditions have been little used. Although specimens of hot-dipped zinc were included in a test of metallic materials in the Bristol Channel [61] there have been few instances of exposure tests of metallic coatings in the sea and in natural water supplies. Much more common is a type of field test designed to determine the resistance of metals to specific liquids, such as brines, acids, alkalies and various other chemicals under the more or less controlled conditions existing in manufacturing or operating processes. While usually employed in comparative studies on metals and alloys tests of this kind are suitable also for testing protective coatings.

In their simplest form, field tests employing immersion of specimens in operating equipment consist in suspending them in a tank or other apparatus which is in operation. A convenient method of carrying out such tests employs what has been described as a spool type of specimen holder.[62] This is shown in Figure 58. The specimens are in the form of discs 2.23 inches in diameter, and are mounted rigidly on the spool in such a way as to be insulated from the metal parts of the frame. When it is desired to study galvanic effects, the insulating spacer may be replaced by a metal dissimilar to the specimen. For example, discs composed of coating and basis metals could presumably be mounted in contact in this fashion. In any case, the test is carried out by placing the assembled spool for various periods of time in the liquid medium (or vapor), the corrosiveness of which is under investigation. Resistance to corrosion is usually determined in terms of change in weight. Visual inspection for pinhole corrosion or rusting should give some indication of the general performance of coated specimens.

A great variety of laboratory immersion tests have been used. Numerous investigators [63] have studied the importance of aeration, temperature, and velocity of liquid about the specimen, and on a basis of these studies, several types of laboratory corrosion test have been developed.[62] In most of these means are provided of controlling the factors given above and other variables, such as solution composition and concentration, and in some cases the character of the atmosphere in contact with the solution. Essential also in attaining reproducible results is the use of a fixed ratio of volume of solution to metal surface area and an arrangement of specimens in the solution in such a manner as to provide a comparable exposure of their surfaces to the solution.

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[60] Hudson, J. C., *Trans. Faraday Soc.*, **25**, 48 (1929); Seeber, R. R., *Symp. on Corrosion Testing Procedures, Am. Soc. Testing Materials*, p. 68, (1937).

[61] Friend, J. N., *J. Inst. Metals*, **39**, 111 (1928).

[62] Searle, H. E., and LaQue, F. L., *Proc. Am. Soc. Testing Materials*, **35**, pt. 2, 249 (1935).

[63] For example, Whitman, W. G., and Russell, R. P., *Ind. Eng. Chem.*, **17**, 348 (1925); Evans, U. R., *J. Soc. Chem. Ind.*, **45**, 504 (1926); Fraser, O. B. J., Ackerman, D. E., and Sands, J. W., *Ind. Eng. Chem.*, **19**, 332 (1927).

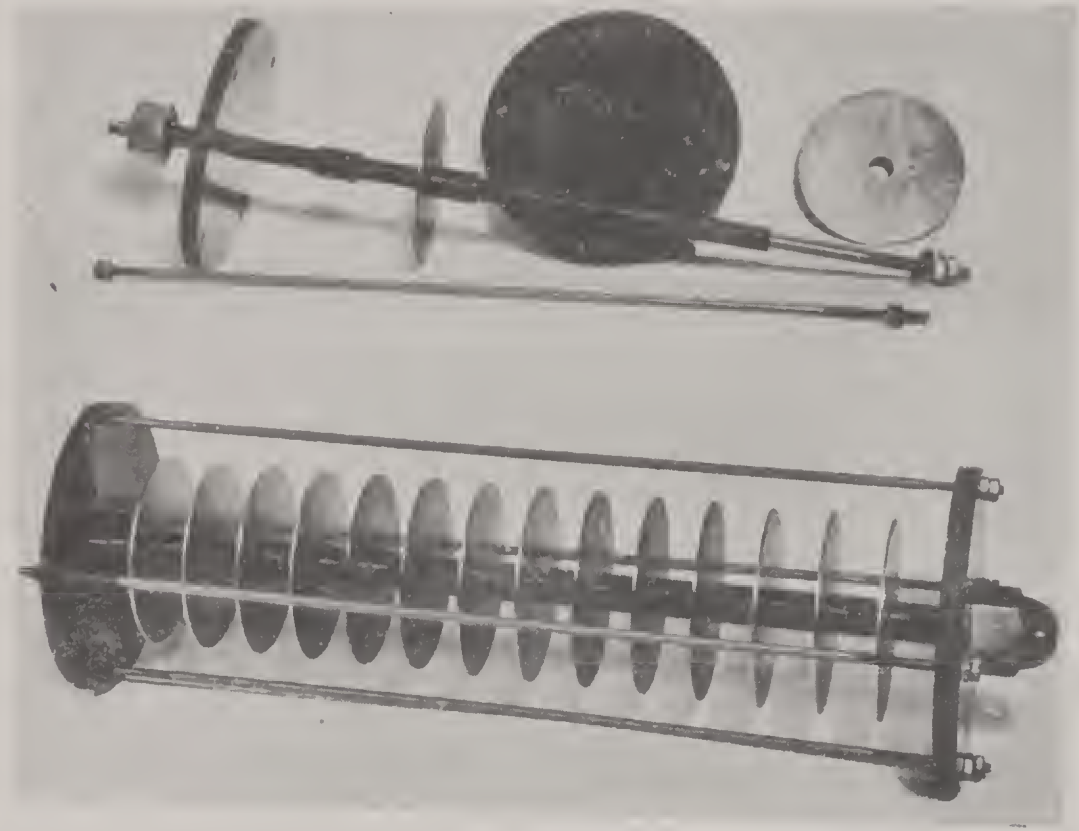

Figure 58.—Spool-type Specimen Holder.[62]

Control of temperature need not be described in detail here. Some laboratories have rooms maintained at constant temperature in which corrosion testing may be carried out. Much more common is the practice of placing the test apparatus in large water or oil baths under thermostatic control. In some cases the heating, cooling, and control equipment may be placed directly in the liquid in which the specimens are immersed for test.

The importance of aeration and velocity in immersion tests lies in the fact that the rate of corrosion is generally controlled by the rate at which either oxygen, or the constituent ions of the solution, reach the metal surface. In solutions exposed to the atmosphere, but not agitated by movement of the specimens or aerated by the production of air bubbles, these chemical components reach the surfaces of the specimens by processes of diffusion or convection. A design for a standard corrosion test has been proposed which provides elaborate precautions for the control of convection currents and other pertinent variables.[64] Ordinary immersion tests, in which the solution is quiescent, generally give test values of poor reproducibility unless special care is taken to control conditions. More consistent results are obtainable when the solutions are highly aerated and some means employed to move the specimens or stir the solution at a constant rate.

Aeration of test solutions may be accomplished in a manner satisfactory for most purposes by forcing air through a porous Alundum or earthenware crucible mounted beneath an inverted funnel[65] or within a glass cylinder open at both ends. The air or gas volume may be controlled and measured by flowmeters. Evaporation losses are usually compensated for by addition of distilled water.

In one type of apparatus[66] the test pieces, supported on glass stirrups and set at an angle to the plane of their orbits, are moved uniformly on a circular path in a vertical plane. This arrangement insures positive flow of solution past every point on the metal surface at some part of each revolution. The apparatus is geared to provide a maximum linear speed for the test pieces of 60 feet per minute. The actual velocity of movement between solution and metal is, however, greater than this value, owing to the angular orientation described above and the impingement of vertical currents resulting from the manner of aeration.

Other types of laboratory immersion test have been devised to meet various needs. More important than any particular design of apparatus or test is the selection and use of procedures which provide proper control of the corrosion rate factors which have been mentioned in the foregoing discussion.[67] There remains the practical difficulty of translating the results of laboratory tests, however well controlled and standardized they may be, into terms of field performance.

Soil Corrosion Testing

The principal metallic coating used for protection against soil corrosion is hot-dipped zinc. It is applied to steel culverts, anchor rods and to a limited extent to iron and steel pipe of smaller sizes. Organic coatings of considerable variety are more commonly used to protect buried pipe lines, and this form of protection is described in Chapter 15. Soil corrosion tests are designed, in the main, for bare ferrous materials and for determining the efficacy of organic coatings, but the performance of zinc, lead and certain other metallic coatings in soils has been investigated.[68] Practical experience, as well as soil corrosion studies, has led to the conclusion that the properties of the soil are more important than the composition of the ferrous metallic material in determining the character and rate of corrosion.[69] Soil corrosion tests are for this reason concerned largely with determining the nature and predominance of the corrosive or protective factors of those environments.

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[64] Bengough, G. D., and Wormwell, F., Corrosion Committee of Iron and Steel Inst., *Third Report*, p. 123, (1935).

[65] Thompson, J. F., and McKay, R. J., *Ind. Eng. Chem.*, 15, 1114 (1923).

[66] Fraser, O. B. J., Ackerman, D. E., and Sands, J. W., *Ind. Eng. Chem.*, 19, 332 (1927).

[67] McKay. R. J., and LaQue, F. L., *Symp. on Corrosion Testing Procedures, Am. Soc. Testing Materials, p.* 87, (1937).

[68] Logan, K. H., and Taylor, R. H., *Nat. Bur. Standards J. Research*, 12, 119 (1934); Logan, K. H., and Ewing, S. P., *Nat. Bur. Standards J. Research*, 18, 361 (1937).

Soils are complex and diverse and provide numerous elements affecting rate of corrosion of buried metals. These may be classified roughly as corrosive or accelerative, and protective or repressive factors. With reference to lead or lead coatings, it is well established that oxygen, nitrates, chlorides and hydrogen ions are examples of the first class, while silicates, sulfates, carbonates and certain colloidal substances fall into the class of protective agents. Both the composition and concentration of these compounds and particularly the ratio of the concentrations of the corrosive to the protective constituents are of importance in determining the character and extent of corrosive attack. The physical texture and drainage of soils affects the concentration and availability of oxygen. Contact of soil particles with a metal surface gives rise to oxygen concentration cells, and it is mainly by means of the operation of cells of this type that metals corrode in soils. In the case of metallic coatings, pores or other coating imperfections comprise an important source of corrosion cells.

From the foregoing it will be evident that an important part of a program of soil corrosion testing is a study of soil properties. Information as to soil type, texture, chemical constituents, rainfall, and drainage, together with service data and field experience on the behavior of buried metallic structures, provide helpful guidance in rating the probable corrosiveness of soils and in the design of protective measures where these are required. Corrosion tests must be relied upon, however, to determine the actual behavior of a metal or metal coating in a given soil.

In its simplest form, a soil corrosion test consists in burying a metallic specimen in the soil in which the investigator is interested. If this interest is broad, both as to materials and soils, the test may approach in magnitude the comprehensive soil corrosion test sponsored in 1922 by the National Bureau of Standards.[70] The procedure of burial usually consists in placing specimens, previously degreased by suitable means and weighed, in a trench from 2 to 3 feet in depth, leaving a space of about a foot between specimens. Cylindrical specimens may be placed horizontally or on end, and sheet specimens should be placed on edge. The earth removed from the bottom of the trench is placed in around the specimens and the trench filled. Enough specimens are employed to permit the removal of sets at the end of successive intervals of time, one, three, five and ten years, etc., and in this way

[69] Logan, K. H., Ewing, S. P., and Denison, I. A., *Symp. on Corrosion Testing Procedures, Proc. Am. Soc. Testing Materials*, p. 95 (1937). This paper contains a valuable resumé of soil testing procedures based upon the authors' extensive experience in connection with the National Bureau of Standards' soil corrosion studies.

[70] Logan, K. H., Ewing, S. P., and Yeomans, C. D., *U. S. Bur. Standards, Tech Papers*, 22, No. 368 (1928).

to determine the rate of corrosion and probable life of the material. Upon removal from the soil, specimens are returned to the laboratory, corrosion products removed by suitable methods, and the loss in weight and depth of pitting measured. It is desirable to protect a small area of the surface of the specimens from attack in order to be able to measure the depth of pitting.

The number of specimens which it is desirable to include in a set depends upon the diversity of the soil. The Bureau of Standards data show that 12 specimens will yield an average having a relative error of not greater than 10 per cent, provided the conditions at the test site are uniform.[69]

In addition to laboratory studies of soil properties, a variety of laboratory soil corrosion tests have been employed in which attempts were made to simulate natural conditions of temperature and moisture. In general, such tests have not provided very dependable information. Much more useful are tests in which the influence of soils on the electrochemical processes of corrosion have been studied. A test cell for this purpose has been described;[71] it consists, as shown in Figure 59, of two steel electrodes separated by a layer of moist soil (containing the quantity of water retained under a centrifugal force of 1000 times gravity), the whole being contained within a brass ring which forms a part of the external circuit. One electrode in the form of a steel screen is buried in the soil; and because of differential aeration it becomes cathodic to a steel disc, the anode, placed on the top surface of the soil separated from the anode by a distance of 2 mm. Electrical connection between the two electrodes is established and the cell maintained in a constant temperature chamber at 30° C. for 18 hours. At the end of this time, the potentials of the cell at different current densities

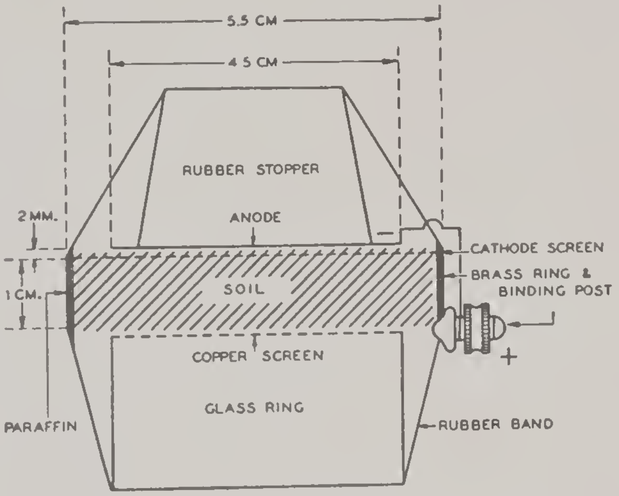

Figure 59.—Diagram of Test Cell for Laboratory Soil Corrosion Tests.[71]

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[71] Denison, I. A., *Nat. Bur. Standards J. Research*, **17**, 363 (1936). See also by same author a description of the test in *Oil and Gas J.*, Sept. 22 (1938).

are measured on open circuit. The average value of cell polarization obtained in this manner has been correlated fairly successfully with pit depth, the relationship being an inverse one. This test should be suitable for studying the behavior of protective coatings.

Accelerated Corrosion Testing

The engineering need of information as to the durability of metallic materials and the relatively long period of time required to secure measurable corrosion results on specimens of these materials exposed to natural environments led to the proposal of accelerated corrosion tests. It was assumed that the rates of reaction might be increased by appropriate means, and that a satisfactory correlation might be established between the rate of the accelerated reaction and the natural rate of corrosion. Many methods of acceleration were suggested which involved an increase in temperature, humidity or concentration of reactants or the application of a "weathering" cycle. After some experience with accelerated testing it became apparent that valid correlations could not be established between these tests and the actual rates of corrosion under the conditions in which the metals were used, and moreover, that the quality ratings established by accelerated methods were often erroneous. However, certain of the accelerated tests, notably the salt spray test and to a lesser extent an intermittent immersion test, became so widely used that they came in time to be adopted as methods of comparing materials and therefore to be useful as acceptance tests.

Salt Spray Test

The salt spray test was first suggested[72] as a method of testing protective coatings on iron and steel to determine their probable performance in seacoast atmospheres. A box or container either of glass, wood, soapstone, or metal suitably finished, is used as the chamber for the specimens, which are suspended or supported so as to permit free access of the mist of the atomized solution of sodium chloride which fills the closed container. The National Bureau of Standards uses a rectangular soapstone box with a glass cover which is held in an inclined position so as to form a reservoir for the solution to be sprayed by the atomizer at the lower end of the box.[73] More recent designs of the spray chamber employed by the Aluminum Company Research Laboratories and the U. S. Army Air Corps are shown in Figure 60.[74] The design of the spray nozzle is shown also in this cut. It operates best at from about 30 to 40 pounds per square inch air pressure and in this pressure range delivers sufficient spray to fill the box. With other types of nozzles lower air pressures are satisfactory. In any case the air should be cleaned by passing through cotton wool and then it should be humidified by bubbling through water. The specimens are best suspended on glass hooks from a rack in the upper part of the box.

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[72] Capp, J. A., *Proc. Am. Soc. Testing Materials*, **14**, pt. 2, 474 (1914).

[73] *Circular No. 80, Nat. Bur. Standards*, (1919).

[74] Dix, E. H., Jr., and Bowman, J. J., *Symp. on Corrosion Testing Procedures, Am. Soc. Testing Materials*, p. 57, (1937); see also Mutchler, W. H., Buzzard, R. W., and Strausser, P. W. C., *Nat. Bur. Standards Letter Cir. No. 530*, July 1, 1938, which contains an excellent review and a new design of spray chamber.

The solution most commonly used is a 20-per cent solution of sodium chloride, although a 3.5 per cent solution appears to be equally corrosive and more easily controlled without deposition of salt.[74] Although the salt spray test is usually conducted at room temperature, it has lately been proposed that higher temperatures be employed. Since the rate of attack is rather markedly influenced, and in some cases the corrosion products modified, by elevation of temperature it seems desirable to control the test at a more reasonable temperature, such as 35° C. (95° F.)

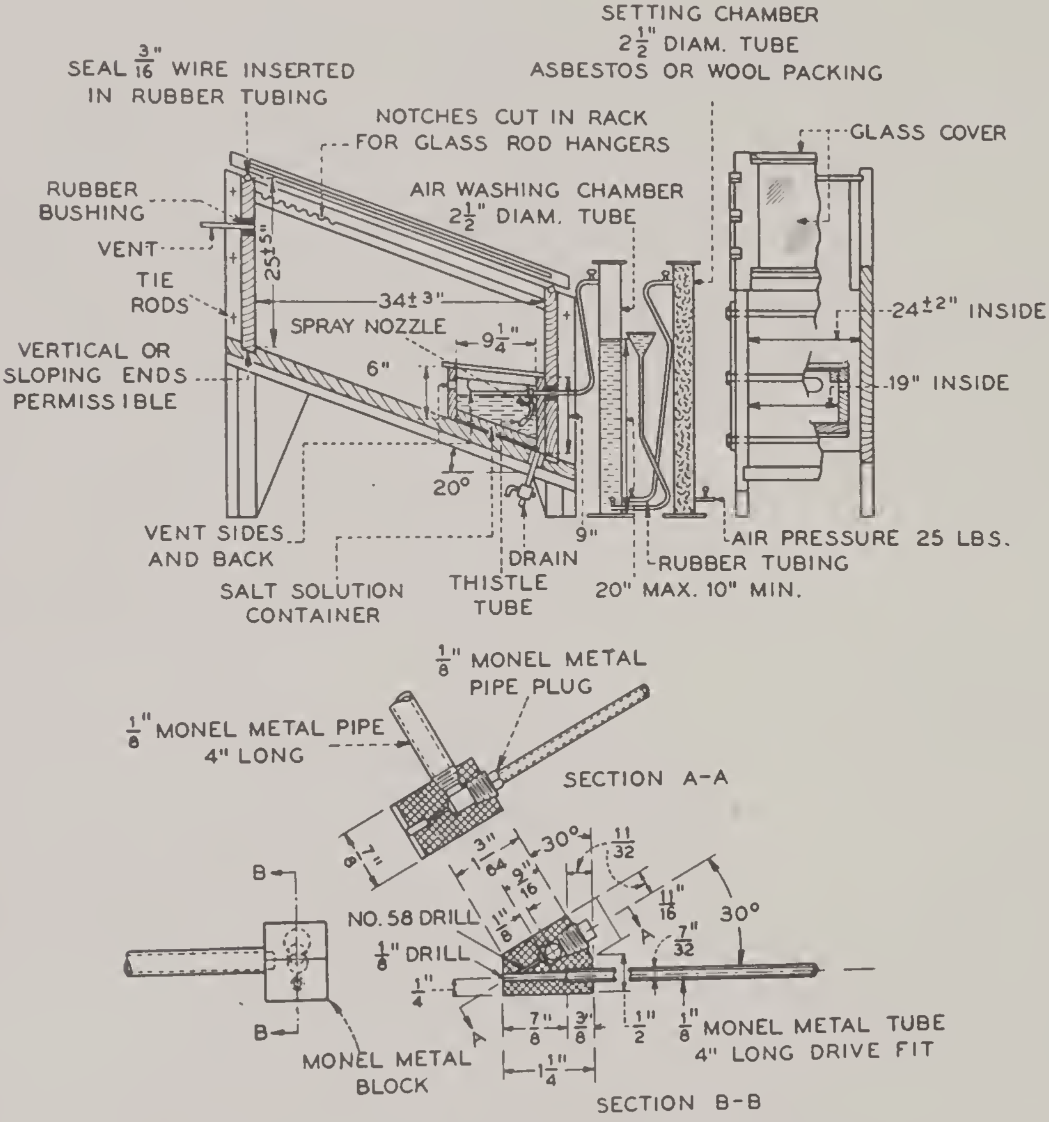

Figure 60.—Design of Salt Spray Apparatus.[74]

The period of exposure employed in the salt spray test varies from a few hours to several months or even years depending upon the material under study. In the case of zinc coatings, it may be profitable to run the test up to 1000 hours, making daily inspections of the progress of corrosion. It has been suggested[74] that it would be advantageous to standardize exposure periods selecting, for example, periods of 100, 500 and 700 hours, 6 weeks, 12 weeks, 26 weeks, 1 year, etc.

The progress of corrosion in the salt spray test is evaluated by visual examination and measurement of change in weight and physical properties. When used either as a porosity test or as a means of determining local thickness of coating, observation of pinhole rusting or rusted areas usually suffices. The most reliable quantitative results are generally obtained from the determination of changes in tensile properties where this is feasible.[74]

The salt spray test has proved a useful means of comparing the quality of different samples of a given material and in some cases of similar alloys. It is unreliable as a test for evaluating the corrosion resistance of different metals and should not be employed for that purpose. It need only be recalled that a few years ago it was concluded on a basis of salt spray test results that coatings of cadmium were superior in general atmospheric corrosion resistance to those of zinc. As is shown in Chapter 7, cadmium coatings are definitely inferior to zinc coatings in all outdoor atmospheres in which comparative tests have been made.

Intermittent Immersion Tests

The intermittent or alternate immersion method[75] is used to some extent as an accelerated corrosion test method for coated metals. The test may be carried out as a series of immersions repeated indefinitely at short intervals or intermittently. In the second case, the interval between two successive immersions is usually made sufficiently long to permit drying of the surface of the specimens.

Several forms of apparatus have been proposed for conducting this test; perhaps the simplest consists in mounting the specimens in a horizontal position on the periphery of a "ferris wheel" so arranged that as the wheel rotates, the specimen at the lowest point is drawn through a shallow tank containing the corroding liquid. More commonly, the specimens are suspended on horizontal rods which are raised and lowered by means of crank-arms at the ends. The motor which rotates the cranks is controlled by means of a suitable timing device so that it is started at chosen intervals and allowed to operate long enough to permit the specimens to be lowered into the solution and then withdrawn into the air. Often the cycle provides 1 minute in the solution and 15 minutes in the air. Where it is desired to induce differential aeration and shorten the time of test, a piece of cotton cord may be placed in contact with the sides of the specimen.[76]

The specimens used in intermittent immersion tests may be standard strip tension test specimens, where the method of evaluation is in terms of loss of tensile strength; or the usual rectangular samples employed in loss of weight studies. Used as a porosity test for nickel coatings[77] or as a local thickness test for zinc and cadmium coatings[17] the specimens are rated according to the extent of rusting.

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[75] Farnsworth, F. F., and Hocker, C. D., *Trans. Am. Electrochem. Soc.*, 45, 281 (1924); Rawdon, H. S., Krynitsky, A. I., and Finkeldey, W. H., *Proc. Am. Soc. Testing Materials*, 24, pt. 2, 717 (1924); Rawdon, H. S., and Krynitsky, A. I., *Trans. Am. Electrochem. Soc.*, 46, 359 (1924).

[76] Crampton, D. K., and Mitchell, N. W., *Symp. on Corrosion Testing Procedures, Am. Soc. Testing Materials*, p. 74, (1937).

Various corrosive solutions have been employed, depending upon metal or coating under test. Among these are 2-per cent ammonium chloride,[77] 20-per cent sodium chloride,[17] 0.5 per cent each of malic acid and sodium chloride.[76] The solutions are used at room temperature and at 35° C., and even up to 60° C. It is usually desirable to control the humidity of the atmosphere in order to obtain comparable rates of drying of specimens tested at different times.

The intermittent immersion test is used less widely than the salt spray test, and is for that reason less important as an acceptance test for coated products. It is said to be more discriminating than the salt spray test.[78] In a recent comparison[17] electroplated zinc coatings failed in about half the time required for failure in the salt spray test although there was little difference in the two tests when applied to hot-dipped zinc coatings.

Sensitive Methods for the Study of Corrosion Reactions

An increasing amount of attention is being devoted to the study of corrosion processes. For this purpose experimental techniques are employed which are sufficiently sensitive to measure the actual rates of reaction occurring in natural environments or under conditions which simulate them. These methods permit the detection of minute quantities of substances and the measurement of their influence upon corrosion reactions. In this way, significant information can be obtained in a reasonable period of time without the danger of distortion introduced by accelerating the corrosion process. Usually, too, the investigator is enabled, as a result of such studies, to understand what takes place and therefore to reach intelligent engineering decisions as to appropriate action. As is well known, ordinary corrosion tests usually require a relatively long time, but a greater disadvantage is that of interpreting the results and applying them to current problems which may involve conditions or metallic materials differing somewhat from those employed in the test. Corrosion tests seldom furnish sufficient information to enable the engineer to predict future performance with assurance. These tests may be supplemented to advantage, however, by studies of the corrosion reactions involved, utilizing some of the methods of high sensitivity which are described in the following paragraphs.

Considerable progress has been made recently in the development of microchemical, electrochemical and spectroscopic techniques capable of detecting microgram quantities of materials. Some of the micro-methods are gravimetric in character, others volumetric and some are based on colorimetry. Electrochemical methods afford an insight into the rate and character of the electrode processes involved in corrosion reactions occurring in the presence of moisture.

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[77] Thomas, C. T., and Blum, W., *Trans. Am. Electrochem. Soc.*, **48**, 69 (1925); Strausser, P. W. C., Brenner, A., and Blum, W., *Bur. Standards J. Research*, **13**, 519 (1934).

[78] Farnsworth, F. F., and Hocker, C. D., *Trans. Am. Electrochem. Soc.*, **45**, 281 (1924).

Microchemical Methods

Micro-methods of chemical analysis have come to be used to an increasing extent in recent years. Many new methods have been developed and micro-techniques have been widely extended. At the Bell Telephone Laboratories more than 35 per cent of all chemical analysis is now done by special methods, many of which are micro-methods. Not only are such methods more sensitive, permitting analysis of small samples, but they are more rapid than the classic methods of analysis when applied to samples of ordinary size. Micro-methods do not necessarily involve the use of a microscope; the term is generally applied to operations involving the use of small samples or low concentrations.

The microscope is a particularly useful tool in corrosion studies where it is necessary to make detailed observation of a corroded specimen and traces of corrosion products. By this means it is often possible to perform identifying reactions on the specimen with a minimum of disturbance and in this way to diagnose the cause of corrosion failures—the most common task of the corrosion specialist or materials engineer.

Micro-gravimetric methods may be applied to the corroded specimen or to the corrosion products; in either case they enable the investigator to determine natural rates of corrosion even in the initial stages. In the selection of specimens for study, a large area per unit of weight is desirable. Micro-balances are generally limited to 20-gram samples, although analytical balances of more robust design may be employed for loads of 100 or 200 grams with comparable accuracy if the Conrady system of weighing is used.[79] This method consists essentially in weighing with the rider adjusted to give a convenient swing and a mean resting point to one side of the zero of the pointer scale, then interchanging weights and object and observing the new mean resting point. Following the second weighing, the rider is shifted until the pointer is carried right across the scale to the position corresponding approximately to that obtained in the first weighing. Weights and objects are again interchanged, and a fourth weighing made which reproduces approximately the deflection of the second. The mean of the four partial weighings yields a result in which errors inherent in the balance completely cancel out. When suitable precautions against drafts, body heat, and high humidity are taken, it is claimed that an accuracy of 1×10^{-8} of the load on the pan, or 0.001 mg. in 100 grams, can be attained. It may be well to point out, however, that Conrady modified the ordinary balance to eliminate sources of error, and that readings of swings were estimated to 0.02 of a scale division.

In the gravimetric determination of a minute amount of a dissolved metal it is customary to resort to reactions in which the metal is precipitated in the form of a salt of high molecular weight, thus incorporating it in a weighable quantity of substance. For example, aluminum may be separated and weighed as the oxy-quinolate, a product which is 18-fold greater than the metal in weight.[80] Another method of weight amplification consists in employing a train of reactions in which the final product is weighable and either contains the metal sought, or is stoichiometrically related to it.[81]

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[79] Conrady, A. E., *Proc. Roy. Soc.*, **A101**, 211 (1922); Vernon, W. H. J., *J. Soc. Chem. Ind.*, **53**, 211 (1934).

Color reactions have long been employed in analytical chemistry as a means of detecting low concentrations of an element. Ordinarily, the technique has been that of comparing the color intensity of a column of solution containing a colored compound of the element under study either with an identical column of a known concentration of the colored compound or with a color standard. Similarly a comparison of turbidity due to the precipitation of traces of an insoluble compound with that of a known standard has been widely used in analysis. Recently improved colorimetric techniques employing paper as a medium have been developed in which the sensitivities of reactions of this kind have been increased markedly.[82]

The use of paper as a medium enables the investigator to confine the reaction to a very small area and in this way to make a chemical analysis of a drop of liquid. The procedure consists in principle in placing a drop of the solution to be analyzed on an absorbent paper and then treating the wet area with a drop of a reagent which will react with a constituent of the original solution and produce an identifiable colored product. If adequate measures are taken to control the area of the spot the quantity of this product can be determined by comparison with calibrated standards. An improvement in the sensitivity of the technique is obtained by impregnating the paper beforehand with a slightly soluble or "fixed" reagent and then introducing the solution under test through the fine tip of a capillary tube. Separation and identification of two or more components by capillary spreading of the solution in the impregnated test paper may be accomplished with rapidity. As illustrated in Figure 61, separation of the components may be based on the precipitation of one component, the difference in solubility of reaction products or on a difference in colloidal behavior. The sensitivity of the capillary burette method is of the order of micrograms.

If the metal under test is present in extremely low concentration in a relatively large volume of solution, as is likely to be the case in many corrosion studies, reagent papers may be employed in a modified technique.[83] This consists in causing the solution to flow through a restricted area of suitably impregnated paper at a controlled rate, the paper being held across the liquid stream between two tightly compressed flanges. The resulting color change may then be compared with standards identically prepared to determine the approximate concentration of metal in the test solution. By this method it is possible in many cases to detect metals present in concentrations of less than one part in ten million.

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[80] Clarke, B. L., and Hermance, H. W., *Bell System Tech. J.*, 15, 483 (1936).

[81] Emich, F., *Mikrochemie*, 13, 283 (1933).

[82] Clarke, B. L., and Hermance, H. W., *Ind. Eng. Chem., Analytical Ed.*, 9, 292 (1937).

[83] Clarke, B. L., and Hermance, H. W., *Ind. Eng. Chem., Analytical Ed.*, 10. 591 (1938).

It is sometimes desirable in corrosion studies to obtain information as to the nature and distribution of impurities in the metal surface and the corrosion products which form at the surface. A convenient and sensitive technique for problems of this kind is that of contact-printing, in which paper moistened with a suitable reagent is pressed on the surface under test. The electrographic method of detecting porosity, described earlier under the section on porosity tests, is a useful method of determining the presence and location of metallic impurities.

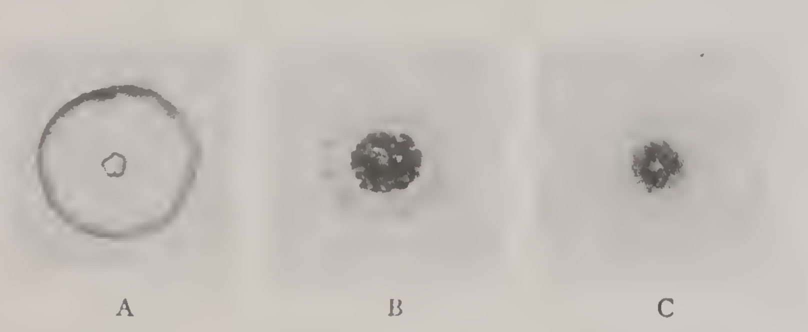

Figure 61.—Three Types of Separations by Capillary Spreading.

A. Separation by precipitation of one component.
Ions separated: Fe (2γ) and Ni (5γ).
Paper impregnant: $BaCO_3$.
$Fe(OH)_3$ precipitated at center. Ni washed to periphery and detected by immersing paper in dimethylglyoxime solution.

B. Separation based on difference in solubility of reaction products.
Ions separated: Ag (2γ) and Cu (3γ).
Paper impregnant: CdS.
Black Ag_2S precipitates at center; brown CuS, having higher solubility product, precipitates in outer zone.

C. Separation based on difference in colloidal behavior.
Ions separated: Cu (5γ) and Fe (3γ).
Paper impregnant: $Zn_2Fe(CN)_6$.
Red $Cu_2Fe(CN)_6$ fixed strongly at center; $Fe_4[Fe(CN)_6]_3$, not readily fixed, diffuses outward with solution, giving blue peripheral zone.

High-vacuum gas analysis methods have been successfully applied to the analysis of thin tarnish films on metals.[84] The tarnished specimen in cylindrical form is suspended vertically in a tube sealed to the gas analysis system. The system is evacuated and a reagent (hydrogen or carbon monoxide) is admitted. The specimen is heated for a few seconds by high frequency induced current during which time the tarnish film is reduced. The reduction products, which may be hydrogen sulfide, water vapor, carbon dioxide, etc., are identified and their quantities determined by means of vapor pressure measurements [85] and chemical reagents. Tarnish films of the order of 5 molecules in thickness may be analyzed by this method with a precision of ± 5 per cent provided the film is of a simple type (oxide or sulfide) and the area of the specimen is of the order of 15 to 20 sq. cm.

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[84] Wooten, L. A., and Guldner, W. G. To be published shortly.

[85] Campbell, N. R., *Proc. Phys. Soc. (London)*, 33, 287 (1921); Sebastian, J. J. S., and Howard, H. C., *Ind. Eng. Chem., Analytical Ed.*, 6, 172 (1934).

Electrochemical Techniques

The electrochemical nature of corrosion reactions occurring in the presence of moisture has been discussed at some length in Chapter 1, where it was shown that the polarization characteristics of corrosion cells largely determine the course of corrosion. As would be expected a knowledge of these characteristics obtained from electrochemical studies usually enables the investigator to determine whether or not a metal is in corroding or corrosion-resistant state. It is of primary importance to know whether a metal is active or passive in a given environment, and this can be determined readily by time-potential measurements, as is illustrated by Figure 6 on page 27. In general, an electropositive (or noble) potential, or a trend of potential in the electropositive direction is indicative of passivity, while a trend of potential in the electronegative direction suggests corrosivity. Two exceptions to this conclusion should be noted. It is conceivable, for example, that if the passivating agent in the environment is inadequate for the production of a continuous non-porous film over the electrode, pits may develop at small local areas without appreciably affecting the composite passive potential of the electrode.[86] Similarly, as shown in Figure 6, the presence of an inhibitor which retards cathodic reactions does not alter the electronegative (or corroding) position of the electrode potential, although the rate of corrosion may be extremely low.

While time-potential measurements do not provide quantitative information concerning rate of corrosion, it is possible from observations of the rate of rise or fall of potential to estimate the comparative behavior of metal specimens in a given environment. It is possible to go somewhat further and determine the relative rates of corrosion of similar metallic materials by measuring rates at which they become passivated in the presence of given concentrations of film-forming reagents. For example, in Figure 62 are given results which have been obtained for the relative rates of sulfation (or passivation) of various grades of lead and certain lead alloys in $7N$ sulfuric acid.[87] It should be emphasized that the relative surface activities of metals determined in this manner can be correlated directly with rates of corrosion only in rather homogeneous environments or where the environment is identical with the medium in which the potential measurements were made. This method of investigating corrodibility should be applicable to the study of protective metallic coatings.

A number of other electrochemical methods have been proposed for the determination of the quality of protective films. In the case of aluminum and its alloys, the amount of leakage current which may pass through anodically formed films is related to resistance to corrosion. The stability of passive films on iron, steel and alloy steels has been investigated by means of potentiometric titration with a chloride solution, observing the amount of chloride required to destroy passive films formed in water and chromate solutions.[88] A number of other investigations of the passivity of ferrous materials in which potentiometric methods were employed has been reported in the recent literature.[89]

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[86] Mears, R. B., (and also Burns, R. M.), *Discussion, Trans. Electrochem. Soc.*, **69**, 181, 182 (1936).

[87] Burns, R. M., *J. Applied Phys.*, **8**, 398 (1937).

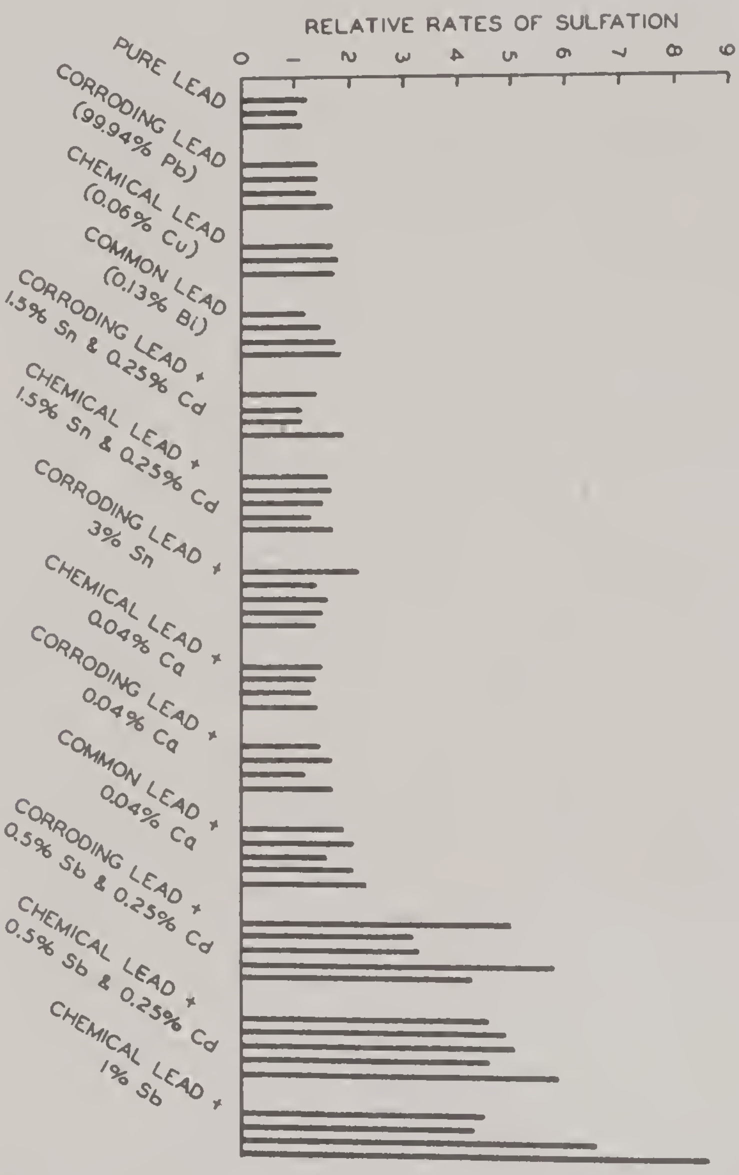

Figure 62.—Relative Rates of Sulfation of Lead and Certain Lead Alloys in 7-Normal Sulfuric Acid.[87]

Potential measurements of the type illustrated above may be made with a potentiometer of ordinary sensitivity. It is of considerable advantage in obtaining a complete record of potential to use an instrument with a recording device attached. In systems in which the electrolytic path is of high resistance, as for example in measurements through paint films,[90] it becomes desirable to employ a more sensitive measuring device and in such cases a vacuum tube electrometer circuit has been shown to be suitable.[91]

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[88] Fenwick, F., *Ind. Eng. Chem.*, **27**, 1095 (1935).

[89] Brennert, S., *J. Iron Steel Inst. (London)*, **135**, 101 (1937); Thyssen, H., and Marechal, J. R., *Rev. Universelle Mines*, **13**, 310 (1937); Yamamoto, Y., *Sci. Papers Inst. Phy. Chem. Research, Tokyo*, **31**, June, (1937).

[90] Burns, R. M., and Haring, H. E., *Trans. Electrochem. Soc.*, **69**, 169 (1936).

A promising method for the determination of rates of corrosion even in the initial stages is a new device of analytical chemistry known as the "polarograph." [92] Essentially it consists of an electrolytic cell comprised of a capillary dropping mercury cathode, a mercury anode of relatively large area and the electrolyte to be analyzed. In operation, an electromotive force is applied to the cell at a constant rate and the resulting cur-

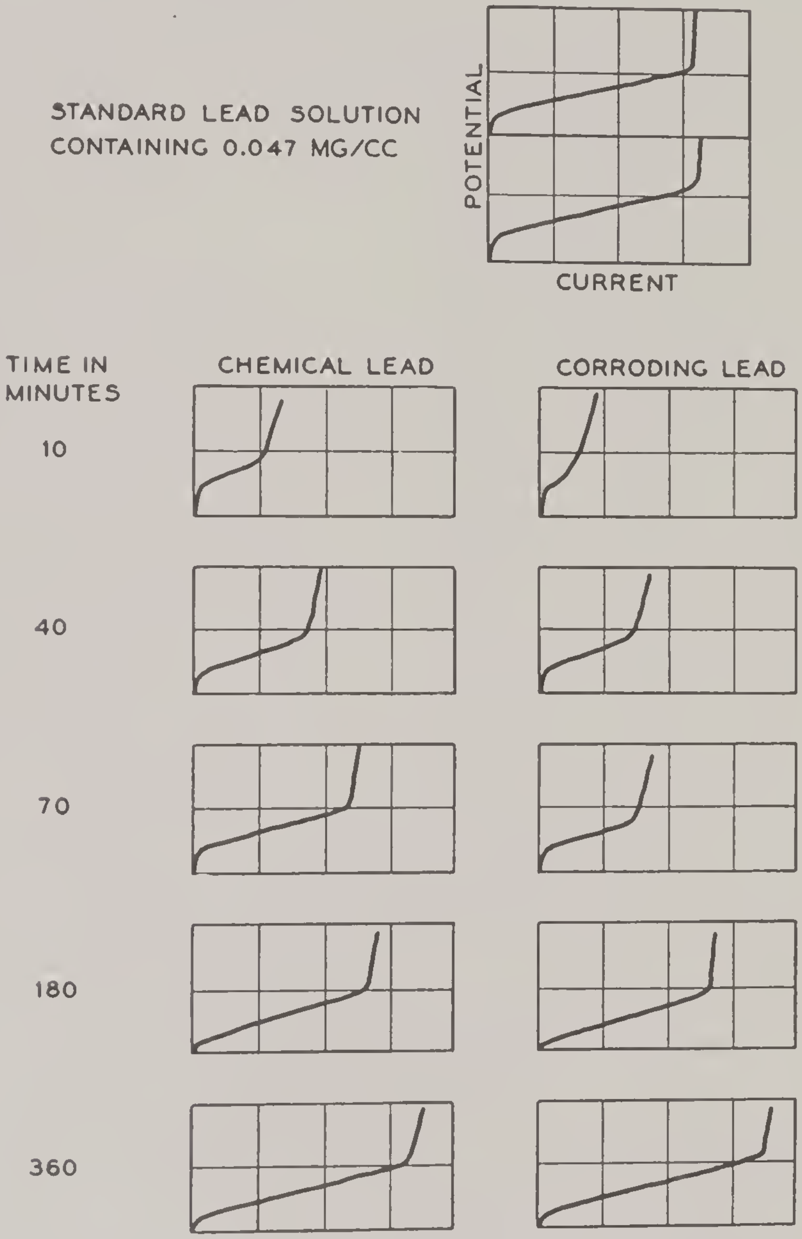

Figure 63.—Polarographic Comparison of Rates of Solution of Two Grades of Lead in Distilled Water at Room Temperature.[87]

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[91] Compton, K. G., and Haring, H. E., *Trans. Electrochem. Soc.*, 62, 345 (1932); Penick, D. B., *Rev. Sci. Inst.*, 6, 115 (1935); *Bell Laboratories Record*, 14, 74 (1935).

[92] Heyrovsky, J., and Shikata, M., *Rec. trav. chim.*, 44, 496 (1925); Hohn, H., "Chemische Analysen mit dem Polarographen," Berlin, J. Springer, 1937.

rent is automatically recorded either photographically or electrically as a function of the polarizing voltage. With increasing voltage, the current rises very slowly until the cathode potential attains a value at which a given positive ion is reduced at the mercury surface. At this point a rapid rise in current occurs which is determined by the mobility and concentration of the ion. By providing a suitable and constant ionic environment with an ion of higher deposition potential, such as lithium, and employing a constant mercury dropping rate and capillary tip, it becomes possible to make rapid determinations of certain metals by comparison with solutions of known concentrations under the same conditions.

In Figure 63 is shown by means of polarographic measurements a preliminary comparison of the rates of corrosion (in distilled water exposed to air) of two grades of lead.[87] The analyses were carried out on the water samples after removal of the lead specimens. It will be seen that initially chemical lead corrodes more rapidly than corroding lead, which result is in harmony with their respective rates of sulfation given in Figure 62. It is of interest to note that after 360 minutes the amount of dissolved metal indicated by the polarograms is nearly the same for both lead specimens, suggesting that the reaction after its initial stages must be controlled by external factors. It is possible by means of this method to determine the concentrations in the same measurement of two or more metals provided their deposition potentials (on mercury) differ by as much as 0.2 volt.

Recently it has been shown[93] that the use of the cathode ray oscillograph in connection with the dropping mercury cathode provides a much more rapid indication of cathodic reactions. In one method this is accomplished by applying a recurrent voltage sweep, in this case 30 sweeps per second from zero to 2.5 volts, to the electrode system and synchronizing the mercury dropping rate with the voltage sweep. Under these circumstances polarographic curves are obtained on the oscillograph which closely resemble those obtained by the slower polarographic method.

The thickness of a thin oxide or tarnish film on metals may be determined by the amount of current required to reduce it.[94] The procedure consists in observing the time required to remove the film from the metal by a constant current when made the cathode in an electrolytic cell. The endpoint is indicated by a more or less sharp rise in the potential of the cell. From the millicoulombs of current required in the reduction process the film thickness may, of course, be calculated. In a modification of this technique, in which the experiment was carried out in a nitrogen atmosphere and the endpoint determined by the break in the cathodic single potential, it has been shown that an oxide film of several molecules in thickness may be present on a metal surface after carefully cleaning and polishing it under benzene.[95]

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[93] Matheson, L. A., and Nichols, N., *Trans. Electrochem. Soc.*, 73, 193 (1938); Muller, R. H., Garman, R. L., Droz, M. E., and Petras, J., *Ind. Eng. Chem. Anal. Ed.*, 10, 339 (1938).

[94] Evans, U. R., and Miley, H. A., *Nature*, 139, 283 (1937).

Optical methods have been shown to be useful in the determination of film-thickness.[96] These consist either in measurements of the interference effects of light reflected respectively from the outer and inner surfaces of the film[97] or the alteration produced by the film in the state of polarization of light reflected from the surface.[98]

The value of the spectroscope in corrosion studies should be mentioned. The detection and quantitative estimation of traces of metallic impurities in metals may lead to an understanding of the corrodibility of certain specimens. Similarly the spectroscope may be used often in examining corrosion products or in detecting traces of certain of the heavy metals which if present, for example, in domestic waters may lead to corrosion problems of various kinds.

Finally, among the newer sensitive techniques of value in corrosion studies, mention should be made of electron diffraction.[99] Considerable success has been achieved with this tool in elucidating the structure and identity of films of corrosion products on metal surfaces.

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[95] Campbell, W. E., and Thomas, U. B., *Nature,* **142,** 253 (1938).

[96] Evans, U. R., "Metallic Corrosion Passivity and Protection," 2nd ed., p. 672, London, Edward Arnold & Co., 1937. This contains an excellent discussion of the application of optical methods to the measurement of film thickness.

[97] Constable, F. H., *Proc. Roy. Soc.*, London, **A, 115,** 570 (1927); 125, 630 (1930).

[98] Tronstad, L., *Z. Phys. Chem. (A),* **142,** 241 (1929); 158, 369 (1932); Tronstad, L., and Borgmann, C., *Trans. Faraday Soc.,* **30,** 349 (1934).

[99] Landau, I. R., *Metals and Alloys,* **9,** 73, 100 (1938).

Chapter 13

Composition of Paints and Mechanism of Film Formation

It has long been customary to employ paints for the protection of metals against corrosion. As in the case of metallic coatings the widespread use of coatings of paint and related organic finishing materials has been an important factor in the preservation of metallic products and structures. Both types of coatings have given rise to large industries, the growth and development of which, in recent years, has been a feature of modern life. Paints protect metals by virtue of the interposition of a continuous, inert and adherent film between the surface of the metal and its environment. Whereas in the case of metallic finishes over metals the electrochemical relationships between environment, coating, and base metal play a predominant part in determining the efficacy of the coatings, such relationships in general play a relatively minor part in the field of organic finishes. Instead, the factors that determine the degree to which the environment can be blocked off mechanically from reaction with the corrodible metal assume major importance. Another general feature of paint coatings in contrast to metallic finishes lies in the fact that the appearance of the finished article is completely transformed, practically any color or combination of colors, surface texture, or degree of gloss being readily obtained. Consequently, organic finishes are applied for decorative as well as protective purposes and any discussion of them must necessarily treat both aspects. Because of their organic nature, these coatings as a class also function as dielectric media and hence find wide application in the electrical insulation field.

As in other fields of material development, we are witnessing in the field of organic coatings an evolution which is remarkable in its scope and celerity. Within the past few decades the field has rapidly changed from an empirical art to a complex and well-founded science. An increasing number of branches of science are exerting their influence to destroy empiricism and replace it with scientific coördination. Unfortunately this tremendous increase of effort is creating a specialized highly-technical group of experts and the adoption of new nomenclatures and concepts not generally familiar. There is a need therefore to evaluate and interpret the recent findings and to apply them to the problem of protecting metals against corrosion.

Paints and related organic finishing materials consist essentially of a continuous inert, film-forming phase in which is dispersed a pigment or combination of pigments. The feature of conversion from liquid to solid phase is essential, both for purpose of applicability of the coating and for the development of an immobilized structure. This structure must adhere to the base solid and be inert to the chemical and physical forces of the environment. The longer it performs this function the better is the paint. This functional definition of any paint in the broadest sense which the nontechnical layman may view it, makes no reference to the chemical composition of the film-forming materials nor to the mechanisms involved in the liquid-solid conversion process.

Historical

The use of paints for decorative or protective purposes goes back to prehistoric times. Paintings in a remarkable state of preservation have been found on the walls of the caves of our prehistoric ancestors in western Europe. They were applied approximately 50,000 years ago and their age speaks well for the technique employed. Functionally, only three components were utilized in these "paints," a continuous binder or vehicle, a colored pigment, and a temporary carrier or thinner for application. The binder probably was a water-soluble root extract, which could change to an inert solid, the pigments were yellow ochres and natural earth reds and the volatile thinner was water. Painting of this character occurred before the age of metals.

At a considerably later point in man's history, the Egyptians developed the art of decorative and protective painting to a remarkable degree. Records of their work have been traced back to 8000 B.C. and it is known that by 1000 B.C. they had developed excellent "varnishes." The composition of these varnishes is not definitely known, but they probably were heated combinations of oils and natural resins, such as the sandarac or mastic type of resin. Pigments of good permanence and wide color array were developed. The coatings were probably applied hot. Although the technique used in formulation and the method of application are obscure, the quality of the work is evident on the mummy cases exhibited in many museums.

In the far East, coating technology was also being developed to a high degree at about this time. Articles coated with oriental lacquers, or so-called japans, applied thousands of years ago, are still in excellent state of preservation. The binding medium or vehicle was a lactiferous exudation from *Rhus vernicifera,* which hardens to an insoluble, infusible film on exposure to a moist atmosphere.[1] From this early period in history, further developments were relatively dormant for many centuries. The first linseed oil varnish was probably developed in the 12th century.[2] During the Renaissance, considerable progress was made in the development of new painting media and pigments. These developments were held as closely guarded secrets by the various famous painters and were limited to nonindustrial small-scale operation. Skilled craftsmen on wood built up varnish-like coatings by a tedious process of applying many coats of linseed oil, with long drying periods and rubbing between coats. With the advent of the industrial era, the scale of operations increased and equipment for making varnishes industrially began to develop. By the end of the last century, commercial varnish plants were operating in which batches of 100 gallon size could be cooked. Linseed oil, cooked with various natural resins to produce varnishes and enamels of varying durability and toughness, was the formulation of that time.

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[1] Oshima, S., *Farben-Ztg.*, 43, 552 (1938).

[2] Miller, R. P., *DuPont Magazine*, 32, No. 5, 8 (1938).

Early in the present century a forward step was taken in the introduction of a new drying oil known as China-wood or tung oil. This oil is considerably more reactive than linseed oil, is compatible with more and cheaper resins, and permits varnish coatings to be made which dry more quickly than similar linseed-oil varnishes, and also show a definite superiority in resistance to water and moisture. This new drying oil led to the development of a new and cheaper type of resin, namely, ester gum, or abietic triglyceride, which was perhaps the first synthetic resin used in varnishes.

At this point, the development of the industry became so diversified that it is possible to touch upon only the high points of this growth. Nitrocellulose had been known since the 1860's and had found limited use as a coating medium, but its high viscosity and the limited number of solvents available prevented its extensive use. After the World War large stocks of nitrocellulose for munition purposes had accumulated in this country and chemists were called upon to find new outlets for the product. It was learned that mild degenerative treatments lowered the viscosity, increased the compatibility, and permitted films of more normal thickness and good protective value to be formed. The modern nitrocellulose lacquers were born as a result of this discovery and perhaps more than any other single development served to stimulate the entire field of organic coating technology. Here was a new coating medium which cut finishing schedules from days to hours. Many industries, particularly the automotive industry, had been retarded by the long period of time required to finish its product. With these new lacquers, the finishing operations could be fitted into the production lines which were being developed so effectively in the mass production industries. Research in solvents, plasticizers, new resins and in methods of application all contributed to expedite developments. A fresh stimulus was furnished to the paint industry to prevent the lacquer type of coating from displacing the slower drying oleoresinous coatings. Research groups were organized and greatly expanded, not only by the paint and varnish manufacturers, but also by the producers of the various raw materials for the paint industry, such as pigments, solvents, synthetic resins, plasticizers, driers, etc. The large consumers found it advisable to establish research groups to aid in the evaluation of the many new developments.

It was fortunate that this expansion of effort was initiated during a prosperous decade of our history, for the value of applied research became definitely recognized during this period and with the turning of the economic tide, scientific efforts in this field were actually increased. The outstanding developments in the past 10 years have been in the field of synthetic resins. Fundamental scientific work has not only developed new resins possessing definite, controllable, and interesting properties, but important insight regarding the resinous state and its relation to the film-forming mechanisms of the organic coating materials. A new era is being ushered in, in which the chemist and his fellow scientists are relieving industry of its dependence on nature for the supply of raw materials. Of considerable importance also has been the development of new and improved methods for evaluating the quality of coating materials.

Classification of Organic Finishing Materials

A recent compilation[3] of raw materials for producing organic coatings lists the physical and chemical characteristics of about 1700 pigments, 260 synthetic resins, 156 different lacquer solvents and 284 available plasticizers. In addition there are listed a number of commercially available drying oils and petroleum thinners. This furnishes an idea of the growth of the paint industry. Obviously, it is beyond the scope of this book to discuss more than a small fraction of these materials. It is more important to attempt to develop a broad picture into which typical representatives of these various raw materials may be fitted and to indicate their functions in relation to the mechanisms that determine satisfactory coatings for protection against corrosion. Paint technology suffers at present from a lack of agreement in terms to designate the various finishing media. With the advent of cellulose derivatives and many synthetic resins within the last twenty years, considerable confusion in terminology has arisen, particularly if the nomenclature of different countries is compared. At the risk of over-simplification, the various organic finishing materials will here be arbitrarily grouped into three general classes, namely, paints, enamels and lacquers. The general composition and the fields of use of these three classes of finishing media will be briefly discussed, after which the components making up these classes, such as the drying oils, resins, solvents, and pigments, will be described.

Paints

A paint consists essentially of a dispersion of a pigment, or combination of pigments, in a drying oil. The drying oil is converted to a gel state, usually by virtue of oxidation at normal temperatures. The oil may be treated in a number of ways to modify some of its characteristics. A drier or a combination of driers may be added to accelerate the early stages of drying. The oil may be partially polymerized or bodied, or else may be fortified by the addition of small percentages of soluble resins, usually synthetic in nature, to increase its film strength and to hasten gelation. In general such modifications entail an appreciable sacrifice in ease of application. Volatile thinners are at times added in small proportions to overcome this defect, even though this may involve some loss in quality of coating. However, the drying oil, usually linseed oil, is still the chief film-forming compound. Drying as a rule is relatively slow and the films formed are soft and readily deformable. With age, progressive hardening occurs, attended by a gradual, definite reduction in distensibility.

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[3] Gardner, H. A., "Physical and Chemical Examination of Paints, Varnishes, Lacquers, Colors," 8th ed., 1937.

The chief use of paints is in the protection and decoration of large fixed structures, where the coating operation is performed at the location of the structure, rather than vice versa. This distinction may seem obvious, but it is nevertheless important, for it has definitely created a number of problems both in formulation and application, as will be brought out later. Unpigmented films of drying oils find relatively little use because of their limited exposure resistance. Paints are usually made by "grinding" the pigments into the oils by differential-speed roll mills, and for certain hard abrasive pigments burrstone mills may be employed. In many instances ball or pebble mills are used. The individual pigment particles are really not "ground," but clusters of them are disaggregated, so that intimate wetting of all the particles by the liquid phase can occur. The gloss of paints is as a rule limited and what little it may initially have is lost fairly rapidly on outdoor exposure.

Enamels

An enamel consists of an intimate dispersion of pigments in a varnish or resin vehicle. The "drying," *i.e.*, the conversion to the gel state, may occur at room temperature by virtue of oxidation, or it may be brought about at elevated temperatures either in the presence or absence of oxygen. Aside from a higher degree of dispersion of the pigment in the vehicle, the essential difference between a paint and an enamel lies in the nature of the vehicle. The enamel vehicle may be an oil-resin mixture, containing either natural or synthetic resins, or it may be a straight synthetic resin medium. The oleoresinous vehicles are commonly known as varnishes. Having drying oil present, they are converted largely by the absorption of oxygen, whereas the newer synthetic resin vehicles may be either oxygen-convertible, heat-convertible, or both, depending on the particular resin used. The enamels as a class dry more rapidly than paints and the coatings are appreciably harder and tougher. With suitable composition the use of heat accelerates the gelation tremendously and at the same time increases toughness and hardness to a point where a vitreous character can be approached. It is in this class of coatings, particularly when baked, that the greatest advances in the organic finishing field are currently being made.

In contrast to paints, enamels are usually applied to structures which can be moved to the point of application of the finishing material. Owing to the finer pigment dispersion and the innate gloss of the dry vehicle, *per se,* the enamels satisfy decorative as well as protective demands. Owing to their resistance to mechanical abuse, they enjoy an increasing use for the finishing of a wide variety of metal equipment used in the home, office and factory. The telephone and other electrical industries finish a large part of their equipment with this class of materials and in the automotive field baked enamels are being increasingly employed.

Considerable skill is required in the manufacture of an oleoresinous varnish. The resins and the drying oils, suitably pre-treated, are brought together under heat and allowed to interact until a compatible, clear and properly-bodied mixture is obtained. Time and temperature must be carefully watched. The various reactions that occur, such as the de-polymerization of the resin, the polymerization of the drying oils, and the formation of cross-polymers between the two, are exceedingly complex. After this high-temperature reaction, the necessary metallic driers and the thinners are added. The cooled varnish is then clarified in centrifuges and stored in large tanks for the purpose of blending successive batches and further slow clarification. It is to the varnish maker's credit that he has been able to control his product as well as he has with the empirical methods he necessarily has been forced to adopt.

In these oleo-resinous varnishes, the ratio of drying oil to resin is of prime importance. In general, with the natural and many of the synthetic resins, the higher the oil content, the more flexible and durable the varnish. Conversely, air-drying speed, initial hardness, and brittleness increase with resin content. However, some of the more recently developed varnishes do not follow this rule. The usual method of stating this oil-resin ratio is by "oil-length," a ten-gallon varnish referring to a varnish in which 10 gallons of drying oil are incorporated with 100 lbs. of resin. Outdoor varnish enamels usually require a varnish having an oil-length of at least 25 gallons of oil for 100 lbs. of resin.

Within the past few years the trend in formulation and manufacture of enamels has been toward simplification. The synthetic resin industry has made available to the formulator various stock solutions having the properties of different oleoresinous varnishes. By suitable selection and blending of these stock solutions, vehicles of the desired characteristics can be formulated without the necessity of cooking. Enamels are produced by the usual dispersion of the pigments in these vehicles, adding the necessary driers in solution form. By way of further assistance pre-ground pigment pastes are now commercially available, which are compatible with these vehicles, thereby simplifying the incorporation of pigments to make the desired enamels.

Lacquer Enamels

A lacquer enamel consists essentially of a dispersion of pigment in a lacquer vehicle. This vehicle is distinctly different from the oleoresinous or oil media, both from the standpoint of composition, formulation and film-forming mechanism. The non-volatile residual film ordinarily contains three components. These are the cellulose ester, usually nitrocellulose, the resin, and the plasticizer, each contributing separate properties to blend into the required overall properties. The cellulose derivative lends strength by virtue of the strong and relatively long, resilient molecules of the cellulose derivative. The strength of a lacquer film is largely dependent on the average molecular weight of the cellulose derivative molecules, which in turn is dependent on the amount that the original cellulose molecule has been shortened by chemical treatment.

For the coating field, a relatively short cellulose-ester molecule must be used; otherwise the viscosity of its solution would be so high that only a very thin solid layer could be laid down in one application. If a film is formed from nitrocellulose, or other cellulose derivatives alone, it would show practically no adherence to the base solid. This lack of adherence is probably more attributable to the excessive shrinkage which a cellulose derivative film undergoes as the last solvent components escape, than it is to the absence of suitable groups that can attach themselves to the underlying solid. Consequently, a resin is added which not only provides adherence and hardness, but also permits thicker films to be deposited. The function of the plasticizer is to contribute distensibility to the film structure by providing a lubricating surface at the micellar walls of the cellulose derivative. At the same time it also contributes to cushioning the shrinkage stresses developed during drying.

Since the mechanism of "drying" of lacquers is dependent on volatilization of the solvents, extreme care in selecting proper solvent combinations must be exercised. Not only must the solvent mixture be able to hold the cellulose ester, the resin and the plasticizer in solution prior to application, but on evaporation, the mixture must be so balanced that at no stage during the escape of the solvent, in the course of which different solvent components escape at unequal rates, is the limit of compatibility of any one of the permanent components exceeded. Such an occurrence would bring about segregation which in turn would prevent homogeneous film formation. A large array of solvents has been made available from which the formulator may select.[4] They vary widely both chemically (esters, alcohols, ketones, ethers, etc.) and physically in their boiling points and evaporation rates.

Owing to their great drying speeds, the lacquer enamels find wide application in the protection and decoration of almost any equipment where spray or dipping application is feasible. In contrast to the paints and enamels, the great majority of lacquers remain permanently soluble in the solvents used for application. This fact, coupled with their speed of setting to a dry film, makes the brushing of lacquers difficult. Even should the evaporation rate be sufficiently slowed down, so that the application of a first coat by brush is possible without too serious lap marks, the application of a second coat by brush over a dry lacquer undercoat is next to impossible.

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[4] For a complete discussion of lacquer solvents, see Durrans, T. H., "Solvents," 4th ed., New York, D. Van Nostrand Co., Inc., 1938.

Clear lacquers are used sparingly for protecting metals. They do find use, however, for tarnish prevention of polished metal surfaces and afford moderate protection on indoor exposure.

The trend in formulation of lacquers and their enamels has been in the direction of increasing the ratio of the resin and plasticizer components at the expense of the nitrocellulose component. Ten years ago a typical lacquer formulation may have employed three times the weight of nitrocellulose to that of resin. Nowadays the ratio would be more nearly reversed. Mixed esters, such as the aceto-butyrates and others, have been developed to bridge the gap between the relatively incompatible cellulose acetate and the highly soluble, but also highly combustible, cellulose nitrate. Furthermore, combination resin-plasticizers are being used increasingly. In these the physical functions of the two components are chemically combined in one synthetically tailored molecule. These formulation trends are definitely reflected in the behavior of the coatings. The modern lacquer might better be called a modified synthetic air-drying varnish, in which the cellulose ester component serves to add toughness and to convert the varnish speedily to a dry film. As a result of this trend in formulation, several of the older inherent defects of the lacquers, such as flammability and susceptibility to photochemical breakdown, have been appreciably mitigated. As might be expected, the behavior and durability of lacquer coatings as a class can vary over wide limits. This will be discussed more fully at a later point.

Organic Finish Components

The broadest classification of the components making up an organic finish would be in terms *vehicle* and *pigment,* the vehicle constituting the continuous phase and the pigment the disperse or discontinuous phase. The vehicle, irrespective of its chemical composition, must possess the property of being able to be converted from a mobile, fluid state to an immobile solid state of a film. The mobile state is obviously necessary for purpose of application of the finishing material, whether that be by brush, spray, roller coat, flow coat, or dip. Just as necessary is the conversion to a film, whether that be by solvent evaporation, by chemical reaction, or by mere cooling. In all cases, a certain kind of solid form must be developed, namely, a "film," in contrast to a crystalline or a non-coherent amorphous condition. It is of importance therefore to inquire into the conditions necessary for film formation.

Film Formation

Although the problem regarding the mechanism of film formation is of long standing and has received voluminous treatment in the literature, it is only relatively recently that a satisfactory simple point of view is evolving which encompasses the several methods by which organic finish films are formed. This point of view may be summarized by stating that the resinous state must be developed before a film can be formed. This resinous state may be preconditioned in the fluid vehicle by virtue of the presence of resin molecules already dispersed in a solvent, or it may be developed in the film after application, owing to the development of resinous molecules by chemical reaction with components in the environment, or by mere heating. This may appear to be begging the question. Actually, however, during the past decade, largely owing to the intensive research on synthetic resins,[5] the conceptions regarding the resinous state are emerging more and more clearly. The primary characteristic of any resin is that it consists of very large molecules. These may have the configurations of long chains, closed chains or chains of cross-linked character. The important point is that the molecules are large. The size of different polymers may range over wide limits, some of the natural polymers being not directly usable for film-forming purposes, owing to excessive dimensions. On the other end of the scale, however, the molecular size must be sufficiently large to fall at least into the lower limit of particle size characteristic of the colloidal domain.

Large size of molecules has attendant upon it two important corollaries. One is molecular complexity. Irrespective of whether the macromolecule is an extended chain, a closed ring, or a cross-linked structure, the opportunity for isomerization as the molecule grows larger, whether by self-addition of repetitive units, or by polycondensation, is increased tremendously. As these molecules grow larger, steric hindrance, wall effects, and local poisons interfere with further growth, and consequently the size of the individual molecules in a given mass of resin necessarily varies statistically over a wide range of values.

The other corollary is that the large size of the molecule automatically associates with it a large molecular surface area. This offers an unusual opportunity for molecular surface forces to come into play. Van der Waals forces at these surfaces can produce solvation, association and aggregation effects, by means of which molecules may associate into micellar structures or in other cases may adsorb foreign molecules with great tenacity. These three conditions, namely, large molecules, complexity of structure and large surface area, characterize the resinous state, which in turn determines solid film formation.

The physical behavior of these resins is primarily determined by the size and geometric structure of the molecules and only secondarily by their chemical composition. In this connection, the work of Carothers[6] and

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[5] For extended discussions of recent developments in the synthetic resin field, the following books are suggested:

Morrell, Barry, Britton, Langton, "Synthetic Resins and Allied Plastics," London, Oxford University Press, 1937.

Burke, R. E., Thompson, H. E., Weith, A. J., and Williams, I., "Polymerization," New York, Reinhold Publishing Company, 1937.

Ellis, C., "The Chemistry of Synthetic Resins," New York, Reinhold Publishing Corp., 1935.

"The Phenomena of Polymerization and Condensation," *Trans. Farad. Soc.*, 32, 177 (1936).

Houwink, R., "Physikalische Eigenschaften und Feinbau von Natur und Kunstharzen," Leipzig, Akademische Verlags G.m.b. H., 1934.

Scheiber and Sändig, "Artificial Resins," London, Isaac Pitman & Sons, 1931.

Staudinger, "Die hochmolekularen organischen Verbindungen," Berlin, Julius Springer, 1932.

[6] Carothers, W. H., *Trans. Faraday Soc.*, 32, 39 (1936); *J. Am. Chem. Soc.*, 51, 2548, 2560 (1929); *Chem. Rev.*, 8, 353 (1931).

Kienle[7] has proved extremely useful. According to these investigators the molecules from which the resin is to be built are examined for their ability to react or join with one another, and Kienle has set up certain workable laws of functionality. Thus for a resin to be formed, the molecules to be joined must each have at least two reactive points. If they have a 2:2 functionality, the polymer will have a chain configuration and will be permanently soluble and fusible, *i.e.*, a thermoplastic resin will be formed. If, on the other hand, one of the reactants has a functionality greater than two, cross-linking occurs and a non-fusible, insoluble, thermal-setting polymer is formed. This three-dimensional interlinking greatly affects the physical structure of the resin, reducing to a large extent the high elasticity characterizing the chain type of structure. Bradley[8] and his co-workers have recently extended the application of Kienle's postulates to the drying oils. By studying the pure drying-oil acids, it has been possible for them to make further distinctions between actual and potential functionality as applied to the heat and oxygen conversion of drying oil resins, and it has also been possible to synthesize products which strongly resemble drying oils in their physical and chemical behavior.

The resinous state is being studied from several other important angles. Within the past few years the kinetics of resinification have been actively investigated and important results may be expected from a better knowledge of the factors determining rate of growth, size, and shape of macromolecules. Infrared spectroscopy is being used to aid in elucidating the resinification mechanism. A large amount of work is being done on ways and means of determining molecular size. Staudinger * and his co-workers have critically examined many polymers and found useful relations between viscosity and molecular size. According to his concepts the high viscosity of chain-type polymers in dilute solution is caused by restriction of free rotation of these long, rod-like structures. With molecules of the interlinked type the molecule grows in three directions and no clear relation between molecular size and viscosity has been found. The ultracentrifuge is being used as a means of throwing additional light on the problem of molecular size. Other investigators have laboriously determined molecular weights of resins by delicate chemical methods based on reactions involving the terminal groups of these large molecules. Both x-ray and, more recently, electron diffraction techniques have been applied to these resins to learn more about their structure.

From the standpoint of the user, the most important aspect of the resin studies lies in the relations between size and structure of the molecules and the physical behavior, particularly the deformation properties of the resin, or films formed from them. In this connection definite progress is being made in clearing up the fundamental relations between elasticity, plasticity and structure of solids.[9] Some workers[10] have shown definite relationships between the average molecular weight of a chain-type polymer and such physical deformation characteristics as tensile strength, impact strength, fatigue resistance, and the moduli of rupture and elasticity. These bulk properties may be expected to be even more sensitively reflected in the film state. Such relations will be deferred for more complete discussion at a later point.

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[7] Kienle, R. H., *Ind. Eng. Chem.*, 22, 590 (1930); *ibid*, 21, 349 (1929); *ibid.*, 23, 1260 (1931); *ibid.*, 25, 971 (1933); *J. Am. Chem. Soc.*, 51, 509 (1929); 52, 3636 (1930).

[8] Bradley, T. F., *Ind. Eng. Chem.*, 29, 440, 579, 1270 (1937).

* See last work given under ref. 5.

With this brief description of the general mechanism of film formation it now becomes desirable to consider the more important materials used in organic finishes. The discussion must necessarily be limited, owing to the large number of individual components and the still larger number of combinations of them in common use.

The Drying Oils

The most widely used drying oil is linseed oil. Next in volume comes Chinawood or tung oil, and then in a definitely lower order of importance at present come such oils as soybean, perilla, and the fish oils. Very recently, oiticica oil is receiving serious consideration as a tung oil substitute. The relative importance of these various drying oils is illustrated in the following table[11] in which the production and import figures (in 1000 pounds) of the several oils used in the paint and varnish industry are listed.

Year	Linseed	Tung	Perilla	Soybean	Fish	All Drying Oils
1932	173,816	59,158	3,226	7,485	7,565	254,251
1934	205,743	88,184	9,898	10,451	11,654	329,894
1936	233,340	94,642	53,222	14,471	35,780	441,282

A number of other plants furnish drying oils which find limited use, and synthetic drying oils may before very long assume importance. In this connection, Scheiber[12] has modified the non-drying castor oil by dehydration and obtained a product comparable to tung oil in its drying characteristics. Although these drying oils may be obtained from widely different sources, they have a number of significant features in common. They are all essentially glycerides of fatty acids having two or more double bonds in a hydrocarbon chain, which is usually at least 16 carbon atoms long. The ability to polymerize, *i.e.*, to form large molecules, is attributed to the presence of the multiple double bonds, and there is good evidence that the relative position of these double bonds is important, since conjugation of bonds increases reactivity.

A large amount of work has been published regarding the drying mechanism of these oils from both a chemical and a physical point of view.

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[9] Houwink, R., "Elasticity, Plasticity, and Structure of Matter," Cambridge University Press, Cambridge, England, 1937.

[10] Douglas, S. D., and Stoops, W. N., *Ind. Eng. Chem.*, 28, 1152 (1936).

[11] Killefer, D. H., *Ind. Eng. Chem.*, 29, 1365 (1937).

[12] Scheiber, J., *Farbe u. Lack*, 361 (1936).

Again at the risk of over-simplification, "drying" of a drying oil appears to proceed as follows. The formation of a solid film is dependent on absorption of oxygen. However, on exposure to air, the wet film does not immediately take up oxygen. The length of this initial induction period appears to be governed by traces of antioxidants in the oils and is appreciably shortened by the addition of metallic driers. The oxygen absorption is considered to form peroxide linkages at the double bonds. During the early oxidation period, volatile oxidation products are split off, among which short-chain aldehydes, acids, oxides of carbon, water, etc. have been identified. Increased drier content furthers the formation of these volatile products. This initial oxidation primarily serves to increase the polarity of the drying oil molecules, which in turn favors the formation of interlinkages with other molecules, with attendant gelation and hence immobile film formation. At this point no further chemical reaction by way of oxygen absorption can be detected. In the case of linseed oil, an amount of oxygen equivalent to twenty per cent by weight may have been absorbed, whereas in the case of a more reactive drying oil, such as tung oil, gelation usually occurs long before such a quantity of oxygen is absorbed. At this stage of drying, an isogel structure in the film has been developed, in which a continuous solid structure is surrounded by a liquid phase of virtually the same chemical composition. Further aging proceeds slowly by way of gradual increase of the solid phase and reduction of the extractable liquid phase. As the latter diminishes more and more, or in Bradley's terminology, as the three-dimensional linking becomes more complete, the film loses high distensibility to an increasing degree and ultimately becomes brittle.

Linseed Oil.—Linseed oil is obtained from the seed of the flax plant which is grown in temperate climates in various parts of the world, *e.g.*, Russia, Argentina, and the United States. The oil is obtained by crushing the seed, followed either by pressing or extraction. Its essential drying components are the glycerides of the unsaturated fatty acids, linolic, $C_{18}H_{32}O_2$, and linolenic and isolinolenic, $C_{18}H_{30}O_2$. In addition, smaller percentages of palmitic, myristic, and oleic acid glycerides are present. As impurities, small proportions of mineral matter are present, which consist of organic complexes of the phosphates of calcium and magnesium as well as quantities of mucilaginous contaminants. For use in paints, the raw oil is treated in various ways to remove some of these impurities, such as filtering, chilling, bleaching with fuller's earth, alkali or acid treatments, etc. So-called boiled linseed oil is made by addition of lead and manganese compounds under heat, which accelerates the drying properties of the oils. Both drying speed and film character are further modified by production of "stand oils," which are partially polymerized drying oils obtained under heat in several ways. If the heat treatment is conducted in the presence of oxygen, the acid value of the oil is perceptibly increased and the iodine value decreased. As a rule these heat-bodied oils show less yellowing in the film than does the non-bodied oil.

Perilla Oil.—Perilla oil most nearly resembles linseed oil in chemical composition and physical behavior. It comprises about 36 per cent by weight of the nuts of the plant *Perilla acymoides,* growing in East India, Manchuria, and Japan. It yellows somewhat more than linseed oil but dries more rapidly, and when heat-treated is more glossy, tough and impermeable to water than an equivalent heat-bodied linseed oil.

Tung Oil.—The drying oil next in importance to linseed oil is tung or "Chinese Wood Oil," obtained from the seeds of *Aleurites cordata,* a tree indigenous to China and Japan. Great Britain, France and the United States have extensive and promising plantings under way, which in a few years more may become important supply sources. The drying component of tung oil is elaeostearin, which at times comprises over 90 per cent by weight of the oil. The greater activity of tung oil as compared to linseed oil is ascribed to the conjugate position of the double bonds in elaeostearic acid. It is used primarily in the production of varnishes and produces films of greatly reduced moisture permeability. It yellows even more than perilla oil, but when it is formed into a stand-oil, this yellowing tendency is reduced.

Oiticica Oil.—Oiticica oil is a drying oil obtained from *Licania rigida,* which grows chiefly in Brazil. It resembles tung oil in behavior and hence is of interest in opening up another potential and important source of raw material. The drying component is now considered to be the glyceride of licanic acid, a γ-keto acid containing three conjugate double linkages in a chain of 18 carbon atoms. It has been found that this oil may at times be substituted for tung oil in tung-linseed oil varnishes, provided the proportion of the tung oil in the varnish is not too high.

Soybean Oil.—Soybean oil, owing to inferior drying qualities, has not as yet found extensive use as a paint vehicle by itself. However, it does show excellent retention of elasticity in the film and yellows very little. Hence its major use at present is in conjunction with other drying oils, or as a constituent for the production of synthetic resins. However, the cheapness and ease of growth of the soybean have stimulated both agricultural and industrial research, as a result of which this may become a very important drying oil.

Fish Oils.—Fish oils have been extensively used for many years as drying oils, usually in conjunction with other drying oils, such as linseed. Improvements in collecting and refining methods have largely overcome the pronounced fishy odor associated with them. In this country, menhaden, a fish similar to, but somewhat larger than, the herring, provides the main source. Other species, such as pilchard, sardine, etc., are also used, and Germany at present is actively engaged in obtaining a drying oil from whales.

One important point to keep in mind regarding these drying oils is their interchangeability. The extent of use of one or another of these oils varies with the price of the raw materials. In most cases, relatively inexpensive chemical and physical treatments can sufficiently modify the various oils to make them serve as satisfactory substitutes for other oils. Table 28 lists several of the properties of these drying oils:

Table 28.—Properties of Drying Oils.

Name of Oil	Specific Gravity	Saponification Value	Iodine Value	Refractive Index	Chief Drying Acid
Linseed	0.9315–45 (15° C.)	192–195	171–201	1.4835 (22° C.)	Linolenic Linolic
Perilla	0.9306 (20° C.)	189.6	206		
Tung	0.9360–432 (15° C.)	193	150–165	1.5030 (19° C.)	Elaeostearic
Soybean	0.9242–70 (15° C.)	190.6–192	124–143	1.4762 (15.5° C.)	
Menhaden	0.927–33 (15.5° C.)	190.6	139–180	1.480 (15° C.)	

Driers

Driers, usually organic compounds of lead, manganese, and cobalt, have been used in conjunction with drying oils and oleoresinous varnishes for many years.[13] They have been extensively studied in order to obtain a better understanding of the drying mechanism of drying oils. Although the exact manner of their functioning is still imperfectly understood, there is agreement on a number of concepts regarding them. Their function is primarily catalytic, in the sense that they accelerate the availability of oxygen to the double bonds of the unsaturated drying oil acids. Only small percentages of them are necessary and although many metals have been investigated, only those forming soluble compounds capable of existing in several states of oxidation have been found effective. Their action has been shown to be primarily related to the early oxidation period of the drying oil, in which an appreciable shortening of the induction period and an acceleration of the formation of the polar groups necessary for film formation have been observed. There is, however, a more lasting effect, in that the character of the film in terms of its physical properties, such as tensile strength and elongation, is affected by the kind and amount of drier used. It is agreed that the cobalt driers affect particularly the surface-drying properties of the oil or oleoresinous medium, whereas the lead and manganese compounds influence rather the through-drying characteristics. Hence, drier balances are carefully watched and are particularly critical in those cases where the coating is subjected to heat during its drying and gelation period.

The linoleates and resinates of the metals mentioned above have been extensively used. However, more recently, other compounds, particularly the naphthenates, are finding increasing use. The latter are relatively pure products readily soluble in the drying oils or varnishes; hence they offer a much improved means of introducing these critical metals in a quantitative manner.

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[13] Elm, A. C., *Ind. Eng. Chem.*, 26, 386 (1934).

Resins

Purely from a standpoint of convenience, resins may be classified on a basis of source, *i.e.*, natural or synthetic. However, as Scheiber [5] has so clearly shown, such a distinction is more academic than real from the point of view of physical behavior. In the final analysis, the definition of a resin, irrespective of its source or chemical constitution, rests upon its performance and behavior. Thus resins may be defined as natural or artificial mixtures of organic substances which are mutually compatible, are soluble in organic solvents at some stage of their development, possess a softening range rather than a sharp melting point, do not crystallize, and when deposited from suitable solvents, form a continuous adherent film. As pointed out earlier, this resinous state is a consequence of the development of large molecules of varied size and shape.

Natural Resins

Natural resins are derived from the exudations of plants, predominantly the conifers growing in many parts of the world. These plants are provided with resin ducts or cavities from which water-insoluble resin flows as a means of protection from wounds, either accidental or man-made. At this stage the resins are relatively fluid in nature, but on exposure, volatile constituents are lost and the remainder undergoes oxidation and a series of complex reactions. In cases of copious exudation, the excess will accumulate on the ground, where it may lie or gradually become buried in the course of many years. Thus there is a continuous transition from the freshly exuded balsams to "recent" resins, recent fossil resins, and finally to the fossil resins. The oldest of these fossil resins is amber, found in oligocene strata of the geologic past. Paralleling this transition is a progressive change in physical and chemical characteristics, beginning with a soft, readily soluble and highly fusible balsam and ending with a hard, almost chemically inert and infusible amber.

It is beyond the scope of this book to discuss the various natural resins in detail. The outstanding commercial example of "recent" resins is rosin, obtained from the exudation of the pine tree after the more volatile constituents have been distilled off. Rosin consists essentially of abietic acid, with, however, sufficient other constituents present to restrain crystallization. It is questionable whether rosin should be classified as a resin, owing to the small average size of its constituent molecules. Furthermore, it finds practically no use directly as a film-forming material, requiring interaction with other materials to form a useful resin. For the paint field its largest exploitation is in the manufacture of ester gum, where by reaction with glycerol, a resin suitable for use in varnish making is formed. Owing to the cheapness and abundance of rosin, a large amount of research is being directed toward finding means to utilize it in the resin and film-forming industry. Abietic acid can be hydrogenated, oxidized, esterified, etc., in order to make resin materials of a wide range of physical and chemical characteristics.

Among the natural resins in which the resinous state is more clearly developed are the elemi resins, obtained as a result of incisions in trees growing in the Philippines and in Brazil. When blended with older fossil resins in the production of oleoresinous varnishes they add toughness, owing to their plasticizing action. Other resins of similar function are mastic, sandarac, and the dammar resins. The resinous state is still more maturely developed in the copals, which frequently are of recent fossil origin. Several varieties of trees growing in various parts of the world, such as the East Indies, South America, Africa and the Philippine Islands, yield the copal resins. As a class, the copals are harder and show more restricted solubility, owing to their greater age. Their properties vary quite widely depending on age, location, etc. They have found extensive use in varnish making and require heat treatment prior to blending with the hot oils to make them sufficiently compatible. In such heat treatment a considerable amount of depolymerization occurs, and a weight loss, owing to volatilization of decomposition products, of 15 to 20 per cent of its weight occurs. The next oldest type of natural resin, which bridges the gap between the copals and the very ancient amber, is kauri resin, obtained from buried exudations from the tree *Agathis australis,* indigenous to New Zealand. Depending on the age of kauri, which may run to thousands of years, the color, and other physical and chemical characteristics vary over fairly wide limits. Again this resin must be heat-treated or "run" before use in the production of a varnish.

As might readily be inferred from this brief discussion of some of the outstanding natural resins, this class of substance shows considerable variation. In order to minimize this, considerable effort is expended in sorting and grading these natural resins. Gross impurities are removed and the resins are graded as to source, color, size and shape of the particles, etc. The varnish manufacturer, however, has been able to utilize this variable raw material to reproduce given formulations effectively, a large measure of skill and intelligent experience being required. It is too early as yet to imply that many of the varnishes made from natural resins are in any way inferior to those made from the more modern synthetic resins. As a result of competition with these recently synthesized products, the chemistry of utilization of natural resins has in the past few years received definite stimulation. By esterification and other chemical treatments, natural resins are being favorably modified, and they are being intensively investigated in conjunction with synthetic resins to modify and improve the latter.

One other natural resin which has been known for centuries and is quite widely used is shellac. Although derived from trees, it is not a plant product, but a resinous material produced by a parasitic insect, *Laccifer lacta,* which feeds on a variety of host trees indigenous chiefly to India. These tiny insects swarm on the twigs of these trees, and come to maturity several times a year, at which times they are collected and scraped off to form seedlac. This seedlac is susceptible to deterioration by exposure to high temperature and humidity, so that short storage periods are advisable. The seedlac is next washed in water to remove coloring matter and other water-soluble impurities. At this stage the seedlacs are graded, inasmuch as there is considerable variation in quality depending on the host tree and the particular crop from it. Orpiment, the sulfide of arsenic, is added to produce a uniform golden coloration. However, it serves no really useful purpose and its use is being rapidly curtailed.

Seedlac can be used directly, but it is common practice to convert it to the varieties of lac commonly known to commerce, such as shellac, garnet lac and button lac. Shellac, the most important of these, is made by drying the washed seedlac in the sun, and then very carefully heating it inside of suitable cloth bags from which it is expressed and subsequently stretched by hand into large thin sheets from which the flaky shellac of commerce is made. Depending on the grade of seedlac employed, various grades of shellac are marketed.

As an organic coating material, either natural or bleached shellac, dissolved in alcohol, finds wide use. It dries quickly, forms hard continuous films which show low permeability and excellent adherence. However, it is quite brittle and hence is restricted to the coating of materials used indoors. Within the past decade, however, shellac has been subjected to intensive study by a coöperative group of scientists, the Indian Lac Research Institute, with laboratories in India, London, and New York. Interest has been focused on the growing of the insects, the methods of manufacture of shellac, and the physical and chemical properties of shellac and modified products from it. Very substantial progress has already been made and it would be surprising indeed if new and important uses for shellac as a coating medium or in other fields were not forthcoming.

Synthetic Resins

A discussion of synthetic resins suitably condensed to fit the scope of this book presents a difficult problem. It is probably safe to say that no class of materials in the history of chemistry has been subjected to as much study at any one period of time as is currently being given to synthetic resins. Literally thousands of chemists are actively engaged in various phases of the field. In the case of many of the newer developments, more time is needed before they can be reliably evaluated.

Notwithstanding the fact that there may be grounds for questioning the general superiority of synthetic over natural resins for use in organic coatings, basically the synthetic resins possess several important advantages. The paint technologist now has in these materials a dependable supply of resin produced from such relatively limitless sources as air, water, cellulose, coal, limestone, salt, sulfur, chlorine, etc. Furthermore, from these plentiful sources can be tailored the molecule necessary to produce the resin which combines just the desired physical and chemical properties for a given use. Important and remarkable as was L. H. Baekeland's contribution to chemistry in demonstrating the controlled resinification of phenol and formaldehyde to an insoluble and infusible state in a period of minutes (a process which nature in the case of amber has not been able to complete in millions of years), his greater contribution perhaps has been in pointing the way toward independence of nature.

At the present time, the two most important classes of synthetic resins in the organic coating field are the phenol-aldehydes and the alkyds. The chief outlet for phenol-aldehyde resins is in the molding field, in which rapid conversion to a three-dimensional infusible molecule is the desired feature. In the paint field, however, compatibility with the drying oil is necessary; hence the resin must be suitably modified. This is accomplished by two general methods: (a) by fluxing the resin with rosin, ester gum and other natural resins to form complexes soluble in drying oils; and (b) by the newer method of employing phenols which contain substituent groups of at least three carbon atoms at the *para* position to the hydroxyl group, producing thereby the so-called "straight" oil-soluble phenolics. Varnishes made of the phenolics are characterized by outstanding durability under those conditions of exposure in which resistance to high humidity, water, and a number of strong chemical reagents is necessary. These phenolic resins are being improved, as indicated by their reduction in yellowing tendency on exposure, which until recently limited their use to the darker-colored shades of enamels.

In contrast to the phenolics, the glyptals or alkyds are almost exclusively manufactured for the paint field. Basically, they are produced by the esterification of a polyhydric alcohol with a polybasic acid. Glycerol and phthalic anhydride were the parent chemicals which have given rise to many related resins. By replacing, for instance, a part of the phthalic anhydride with drying oils, drying oil acids, natural resins, other polycarboxylic acids, etc., a wide variety of synthetic resins is made. These differ greatly in their physical characteristics, as do the resultant films made from them, either with or without drying oils. They can be made to produce coatings that are converted to the solid gel state with or without oxygen and with or without heat. The heat-converted films particularly are characterized by having attractive combinations of desirable properties such as toughness, non-yellowing, chemical stability and durability.

A number of other synthetic resins are receiving attention for use in the organic finish field. In fact, it may be said that although the synthetic resin field is primarily concerned with the development of plastics, every new synthetic macromolecular substance is seriously examined for its possibilities as a coating medium. Thus there are the various vinyl derivatives, such as polystyrene, polyvinylacetate, the co-polymers of vinyl acetate and chloride, the vinyl aldehydes, and most recently the acrylic acid derivatives. Each one of these is finding a definite field for itself by virtue of having unique properties in addition to satisfactory overall characteristics. As a class these vinyl resins have excellent color stability and high adhesion. Their moisture permeability is low and mechanically they form tough films. The polystyrenes have unusual electrical characteristics, namely, low dielectric constant and low power factor loss over a very wide frequency range. The acrylic acid derivatives are characterized by remarkable clarity and color stability. No one resin combines all the desirable characteristics to a superlative degree, yet each one is serviceable for a large number of uses.

In the past few years considerable effort has been devoted to the formation of cross-polymers, *i.e.*, hybrid resins in which it is attempted to combine favorably the desired properties of several individual classes of resins. Thus hybrids between the alkyds and the phenolics, as well as the urea-formaldehyde resins, have been developed. As may be readily appreciated, the possibilities are numerous and it is in this recent trend of hybridization that more study will be required before the quality of the material can be determined with assurance. It is probably easier to degrade a product than to improve it, and mere cross-polymerization *per se* offers no assurance of improvement in quality. Very recently, modified urea resins in combination with alkyds have created considerable interest because of their high speed of gelation on baking, the conversion being completed in a fraction of the time usually required by other baking materials.

A number of other synthetic resins have been developed for the coating field. Among the older types are the coumarones and indenes. Olefins from the petroleum refinery have been polymerized. Rubber has been depolymerized by treatment with chlorine to yield chemically inert resins. Another product of nature which has received intensive study is cellulose. The derivatives of cellulose are difficult to classify as resins, for although they possess most of the characteristics of resins they do not lend themselves to the formation of adherent films. Cellulose derivatives require an appreciable amount of depolymerization of the parent polymer, native cellulose, in order to attain the desired solubility and film-forming properties. The outstanding members of this family are cellulose nitrate, cellulose acetate, mixed esters, such as cellulose acetobutyrate, and the cellulose ethers, of which the ethyl ether has been developed to the greatest extent in this country. In this family again, no single member is without certain disadvantages. The nitrate is inflammable and "yellows" appreciably, the acetate exhibits too limited a compatibility to find use as a general lacquer material and ethyl cellulose is as yet too new a product to have been completely appraised.

Pigments and Pigmentation

As has been indicated, unpigmented organic coatings find only limited use as protective coatings for metals. The addition of pigments introduces a number of highly important changes in these clear coatings. First of all, the property of coloration and of capacity for obscuring the underlying base material is imparted. The choice of color or color combination is practically unlimited and the application of an organic coating of the order of a thousandth of an inch in thickness completely transforms the appearance of an object. By the addition of pigment the organic coating is strengthened, hardened and made relatively much more durable. The deleterious effects of certain environmental factors are delayed by pigmentation. For example, the rate of moisture permeation is reduced, and in some instances, the destructive action of ultraviolet light rays is minimized. The presence of pigments allows the development of "body" in the paint, so that vertical and uneven surfaces can be coated to a smooth appearance. By incorporation of suitable pigments in the priming coats of multiple paint coatings, the corrosion of the base metal may be retarded—a result which is discussed at greater length in Chapter 14.

Pigments come from many sources, a limited number being obtained as direct natural products. In this class are the natural earth pigments, such as the ochres, siennas, umbers, etc. These natural earth pigments consist mostly of iron oxides, admixed in varying degrees with manganese, other oxides, silicates, etc. A number of the natural deposits have been prized for centuries for the quality of their pigments with respect to color, stability, uniformity of particle size, opacity and inertness in most paint vehicles. The majority of pigments, however, are manufactured. A large number of these consist of insoluble inorganic precipitates, others are produced by solid-gas reactions, and still others by precipitation or mordanting on an inert supporting base. In all cases, a high order of manufacturing control of the various processes has been developed.

It is not possible within the scope of the present work to discuss individually the vast number of pigments employed in the preparation of paints. It is proposed instead to consider the properties common to most pigments. For the most part, paint pigments are insoluble, chemically inert substances. Although the hydrogen-ion concentration of their aqueous dispersions may show values of pH ranging from 3 to 9, more commonly the value approaches pH 7. The amount of water-soluble matter in pigments is of the order of a trace. In paint technology, pH values deviating from 7, particularly on the alkaline side, are important, owing to the protracted opportunity on exposure for reaction with acidic constituents in the vehicle. Mildly alkaline pigments may actually be helpful, but a limit of permissible alkalinity is quickly reached. Following is a list of electrometrically determined pH values of a limited number of pigments.[14] These values represent determinations on one sample only of each pigment; other samples may show different values.

One of the outstanding characteristics of practically all pigments is their fineness of particle size. The majority of them fall between a range of 0.1 to 5.0 microns in average diameter. Thus it would be possible in a paint film of ordinary thickness for approximately a hundred pigment particles to lie one on top of another. The presence of particles of this size

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[14] Gardner, H. A., "Physical and Chemical Examination of Paints, Varnishes, Lacquers, Colors," 8th ed., p. 650, 1937.

Whites	*pH*
White lead, carbonate	5.9
White lead, sulfate	6.2
Lithopone	7.0
Lithopone, high strength	8.8
Zinc sulfide	6.6
Titanium, barium	7.5
Titanium, calcium	7.0
Antimony oxide	4.2
Blacks	
Lamp	3.6
Carbon	6.8
Graphite	7.2
Bone	9.2
Colors	
Chrome green	5.5
Chrome oxide green	6.7
Chrome oranges	5.9–7.5
Hansa yellow	7.0
Indian red	7.3
Iron oxide	6.0
Para red	8.0
Red lead	8.3
Zinc chromate	6.6
Toluidine red	6.4
Sienna, burnt	6.6
Umber, raw	8.0
Extenders	
China clay	6.8
Blanc fixe	8.5

provides a large surface area. Whereas a solid cube, one centimeter on an edge, has six square centimeters of surface, the same material reduced to cubes 0.1 micron on an edge develops sixty square meters of surface. With such increase of surface area, interfacial properties at the pigment-vehicle surface become extremely important. The wettability by the binding vehicle is directly determined by the chemical character of the pigment surface, and these wetting characteristics affect not only the ease of dispersal and the stability of the dispersion, but also the type of failure of the coating which occurs upon exposure to the environment. Thus, pigments of alkaline character are wetted readily and for this reason definitely affect the physical structure of the paint film. Other pigments are difficult to wet completely and this accounts to a considerable extent for the chalking tendencies of coatings containing them. A number of patents have been granted within recent years in which the poorly wetting pigments are coated with exceedingly thin films to modify their dispersion behavior and their subsequent behavior upon exposure.

In addition to particle size, the shape and the statistical distribution of both size and shape of the particle affect the behavior of paint films.

This distribution determines to a large extent the packing arrangements of the pigment particles in the dry film, and this in turn affects the ease of moisture transfusion and the distribution of minute physical stresses which are incident to such effects as progressive shrinkage of the binding medium or changes in temperature and humidity. With certain pigment combinations it has been found highly beneficial to select the pigments in such a manner that the development of large stresses can be avoided. Under such circumstances the paint, instead of failing by the gradual development of deep conspicuous cracks, is gradually eroded as a consequence of the development of a multitude of microscopic cracks. This behavior provides a suitable surface for repainting. The foregoing method of controlling the type of failure by proper pigmentation has been highly successful, particularly in the house-paint field, where controlled chalking has prolonged the satisfactory appearance as well as the life of the coating.

It has been found that the ratio of pigment to vehicle is important. Wolff [15] and his collaborators investigated this relation in connection with the brushing characteristics of paints and have found that it has an important bearing on the durability of the coatings. An optimum value for pigment concentration has been established and for a large number of pigments this lies between a value of 25 to 35 per cent by volume of pigment.[16] Fortunately this is approximately in the range of optimum consistency for application of most pigments, and hence a useful relation between durability and pigment content is furnished at a convenient point of formulation of a new paint. These considerations are particularly important in the case of top coats. In priming coats, when inhibitive pigments, such as chromates or red lead, are used, the added electrochemical protection offered by these pigments offers somewhat more latitude in variation of pigment content.

Another desirable characteristic of pigments is their ability to exclude ultraviolet light, which at wavelengths below 4500 Angstroms produces increasingly deleterious effects on the binding medium. The following table [17] lists the light transmission characteristics at 3655Å of a number of pigments.

Here it is seen that highly transparent pigments do not exclude ultraviolet light until a layer approximately 0.002 inch thick has been built up, which is slightly less than the thickness of an average two-coat paint job. The opaque pigments on the other hand do not allow ultraviolet light to penetrate into the paint coating more than approximately 0.00005 inch deep, or the exterior twentieth of an average single coat of paint. This ability to exclude ultraviolet light is related to the chalking tendencies of a coating. Thus poorly wetted pigments, coupled with high ultraviolet light transmission, chalk badly, whereas well wetted pigments, coupled with high

[15] Wolff, H., *Farben Ztg.*, **37**, 374 (1932); Wolff, H., and Zeidler, G., *Kolloid Z.*, **74**, 103 (1936); *Farben Ztg.*, **40**, 667, 693 (1935); *ibid.*, **42**, 357, 383, 439 (1937).

[16] Elm, A. C., *Ind. Eng. Chem.*, **26**, 1245 (1934).

[17] Nelson, H. A., and Norris, W. C., "Pigments in Nitrocellulose Lacquer Enamels," Research Bulletin, New Jersey Zinc Co.

Table 29.—Transmission of Ultraviolet Light by Pigments.

	% Transmission at 3655 Å of .00092 mm. layer	Extinction Thickness (in mm.) at 3655 Å
Basic lead carbonate	61	0.0270
Lithopone (30% ZnS, 70% $BaSO_4$)	43	0.01
Titanium dioxide	18	0.0046
Zinc oxide	0	0.0009
Zinc sulfide	22	0.0062
Asbestine	90	
Barytes	65	
Silica	85	
Carbon black	0	0.0006
Prussian blue (10% $Fe_4[Fe(CN)_6]_3$	40	0.0055
Sublimed blue lead ($PbSO_4$ 50%, PbO 38%, PbS 6%)	8	0.0021
Ultramarine blue	85	0.0523
Chromium oxide (98%)	10	0.0022
Chrome yellow ($PbCrO_4$ 65%, $PbSO_4$ 35%)	0	0.00085
Chrome yellow (98% $PbCrO_4$)	4.5	0.0015
Zinc chromate (100%)	32	0.0030
Orange mineral (93% mineral oxide)	55	0.0077
Iron oxide (98%)	0.5	0.00095

opacity, do not chalk. Zinc oxide is of the latter class, whereas basic lead carbonate approaches the former. Carbon black, on the other hand, although highly opaque, frequently chalks badly owing to poor wetting. These relations between wetting, ultraviolet light transmission and the resultant chalking suggest a method of measuring effective adhesion between pigment and vehicle, inasmuch as both light transmission and amount of chalking can be quantitatively followed.

For a number of reasons, paints are usually compounded with several pigments rather than with single pigment species. There is no single pigment that serves all purposes. Reactive pigments may be used for priming protection or for hardening and strengthening of the film. Non-reactive pigments may be used for coloration, for stress-easing purposes or for retention of elasticity of the coating. Other pigments may have the particular virtue of excluding ultraviolet light or of reducing permeability to moisture. It has been learned that the admixture of several pigments, particularly in top coats, is frequently accompanied by a "symbiotic-like" effect, in which the several pigments exert a mutual benefit to improve the entire coating.

From the standpoint of the protection of metals against corrosion, the pigments used in the coat of paint immediately adjacent to the metal are important. Since these priming-coat pigments are intimately related with the entire performance of a protective paint coating, these will be reserved for discussion in the following chapter.

Chapter 14

The Durability and Evaluation of Paints

The life of a paint coating on a given structure depends upon a large number of variables. There is first of all the character of the paint medium employed, that is, whether it be a drying-oil paint, enamel, lacquer, or some other vehicle. Then there is the question of the kind of metal to be finished and its surface condition. If the painting is to be conducted outdoors, the meteorological conditions during painting, or immediately thereafter, have a definite bearing on the life of the paint coating. In addition, there are long-time exposure factors which must be considered. If the coating is to be exposed outdoors, the temperature, humidity, intensity of sunlight, air pollution and the extent of variation of these factors all play a part. If buried underground, the finish will be subjected to soil waters bearing a variety of constituents, to pressure and abrasion by soil particles and to destruction by bacteria, insects and rodents. All of these conditions influence durability, and the selection of a given paint or paint system at best can merely strike a favorable compromise.

The nature of the object to be coated dictates to a large extent the level of durability to be sought in the coating. For large structures, such as bridges, gas tanks, etc., the economic balance obviously favors maximum life of the coating, owing to the relatively large cost of the structure and the high cost of applying the paint coating. On the other hand, many small articles of relatively low intrinsic value may be adequately finished with coatings having only a short life.

Factors Determining Durability

Within the past few years an increasing appreciation has developed of the underlying mechanisms by means of which the failure of a paint coating may occur. Reduced to its barest essentials, the function of any protective paint coating is to prevent corrosion of the basis metal in the environment in which it is used. If a paint coating is perfectly continuous and chemically inert in the environment, and at the same time possesses mechanical attributes which enable it to withstand external stresses incident to its exposure or service, it has a good opportunity of fulfilling its function. A finish must adhere not only initially but for a relatively long time. The average thickness of a single coat of paint is of the order of 0.001 inch. A good quality, exterior protective paint system usually consists of three coats of paint. Cases are on record where such paint systems over steel structures have lasted for decades without requiring much further attention. Sabin[1] mentions a railroad bridge which after 46 years was still in excellent condition, although it had been repainted only once. D'Ans[2] points out that the finish on the Cologne railroad bridge has performed satisfactorily for fifty years. Although these examples perhaps illustrate outstanding performance records, it is nevertheless remarkable that organic coatings, only a few thousandths of an inch thick, can furnish such protection.

The fundamental mechanisms involved in the degradation and failure of paints are concerned with certain electrochemical aspects of the priming coats, with various factors which determine both initial and retained adherence, with the behavior of these coatings toward moisture, corrosive gases and other environmental influences, and finally with changes in the internal physical structure of the coatings, as determined by composition and influenced by application and exposure conditions. It should be emphasized that the interrelation between these factors is more important than the factors themselves. Only rarely does a paint coating fail primarily by a single mechanism, and usually the concomitant action of several factors is involved. Progress in paint technology depends to a large extent on a clearer understanding of these mechanisms and their interrelations.

ELECTROCHEMICAL ASPECTS[3]

In the opinion of many investigators the primary function of a paint coating is one of mechanical exclusion of the environment from the metal surface. However, in the priming coat, that is, the paint coating next to the metal surface, electrochemical factors unquestionably play a part. Whether the incorporation of a corrosion inhibitive pigment in the primer forms a "secondary" or "primary" line of defence is perhaps not important. It is known that certain pigments exert an inhibitive action at the metal interface and definitely promote the retention of adherence.

The surfaces of virtually all the metals and alloys in commerce are characterized by inhomogeneity. This lack of homogeneity furnishes the seat of electrochemical forces. The distribution of anodic and cathodic points, lines and areas varies widely, depending on the composition and the thermal and mechanical history of any given specimen. The flow of electrical current necessary to permit electrochemical attack obviously requires a closed circuit between the anode and cathode elements. Stopping the flow of current at either anode or cathode, or eliminating the ionic conductance between anodic and cathodic areas, prevents corrosion. The organic binding medium in a paint by its inherent nature retards ionic conductance. The degree to which it can do this is dependent on its moisture sorbing characteristics, and on the number and kind of conducting ions which either it or the dispersed pigment can make available on moisture sorption.

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[1] Sabin, A. H., "Red Lead and How to Use it in Paint," p. 44, New York, John Wiley & Sons, 1920.

[2] D'Ans, J., *Farb. Ztg.*, 43, 210-211, 245-246 (1938).

[3] The following works discuss the theory of corrosion as related to the paint problem:
Jordan, L. A., and Whitby, L., "Preservation of Iron and Steel by Means of Paint," Bulletin 16, Paint Research Station, Teddington, England.
Matthijsen, H. L., *Verfkroniek*, 10, 165-72, 189-95, 208-13 (1937).
Ragg, M., *Verfkroniek*, 10, 26 (1937).
Vernon, W. H. J., and Jordan, L. A., *J. Soc. Chem. Ind.*, 50, 1050 (1931).
Nelson, H. A., *Ind. Eng. Chem.*, 27, 35 (1935).
Evans, U. R., "Metallic Corrosion Passivity and Protection," pp. 584-629, London, Edward Arnold & Co., 1937.
Speller, F. N., "Corrosion Causes and Prevention," 2nd ed., New York, McGraw-Hill Book Co., Inc., 1935.

In the case of iron or steel, metallic iron enters solution as ferrous ions at the anode. The ease with which iron dissolves at the anode is determined by several conditions. One of these is the hydrogen-ion concentration immediately adjacent to the metal surface. The more acidic the medium, the more readily iron dissolves, and conversely, the more alkaline the immediate environment at the anode, the less the tendency of iron to enter solution. Hence, priming coats containing pigments which produce an alkaline condition next to the metal surface retard or prevent anodic attack. If the ferrous ion is quickly oxidized to the ferric condition, the slightly soluble ferric hydroxide is precipitated in close contact with the metal surface, thereby stifling further anodic attack. When a strong oxidizing agent, such as the chromate ion, is available at the metal surface, this stifling action is more pronounced and, as shown in Chapter 1, the metal surface becomes passivated.

The primary reaction at the cathodic areas of corrosion cells has been shown to be the conversion of hydrogen ions to hydrogen atoms, which, so long as they remain on the metal surface, give rise to a polarized condition and thereby reduce the current flow in corrosion cells. With the discharge of hydrogen ions, the immediate vicinity becomes alkaline, owing to a surplus of hydroxyl ions. If there are present in the immediate environment alkali or alkaline earth metal ions (as for example sodium, potassium and calcium ions) the hydroxyl-ion concentration may become very high. At pores in the paint coating (which will be cathodic areas), the local alkalinity developed in this manner may become sufficient to produce, by reaction with the acidic components of the organic vehicle, a condition known as "alkaline peeling." This action may extend to areas considerably larger than the original pore.[4]

It has been pointed out that chromates inhibit attack by anodic control, that is, by passivating anodic areas, and this is the case in neutral or alkaline environments in the absence of high chloride-ion concentrations. However, in acid environments, such as prevail in the atmosphere of industrial districts, chromate pigments are likely to accelerate corrosion by oxidizing and thereby removing the film of hydrogen which surrounds and polarizes the cathodic areas.

There are other evidences that the electrochemical phenomena at the primer-metal interface play an important part. Thus the more active metals or metal alloys, such as zinc, aluminum and magnesium alloys, in severe environments generally require chemical surface conversion treatments to reduce the activity of these metals. Whereas for steel the lead pigments, particularly red lead, are strongly inhibitive, in the case of these more reactive metals, lead pigments have been found stimulative. Also, the carbon pigments over steel stimulate corrosion, owing to the high potential between iron and carbon. Aluminum pigments find use mostly in top coats over various metals. The aluminum pigment is ordinarily covered with sufficient oxide so that it performs essentially as an inactive pigment. However, in salt water, aluminum pigment has been adopted as a priming coat for steel by the U. S. Navy,[5] and it is claimed [6] that in this environment the normal protective film on the aluminum particles is broken down, and that as a result the metal protects the underlying basis metal electrochemically in a manner similar to the sacrificial protection offered by metallic zinc dust powder in paints on atmospheric exposure.

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[4] Evans, U. R., *Trans. Electrochem. Soc.*, 55, 243 (1929).

Pigments Used for Corrosion Protection

For a number of years, a relatively limited number of pigments have found extensive use in corrosion resistant paints. In the priming coats, the electrochemical action of such pigments dispersed in paint vehicles is important. In general, the paint used in priming coats requires protection by top coats. It so happens that the priming coat material, although satisfactory for corrosion protection at the interface, is frequently not satisfactory for top coats. Its color, its stability toward weathering, or its physical durability may be unsatisfactory and hence top coats of different composition are almost invariably used.

Red Lead

Of all the pigments that have been used in primers on ferrous metals, red lead has the best overall record. It has been in constant use for well over a century, and in all carefully conducted paint studies has always ranked very high. It is not meant to imply that there is no other priming pigment better than red lead, for unquestionably several other pigments have in specific instances given superior protection. However, it is the one priming pigment which has consistently shown up well both in tests and in actual practice.

Red lead is made by roasting litharge, PbO, at temperatures between 600 and 700° F. Depending on the structure of the litharge and the roasting conditions, a red lead containing varying amounts of Pb_3O_4 is formed. At present the American Society for Testing Materials is standardizing on three grades of red lead, namely, the 85, 95, and 97 per cent grades, the percentages signifying minimum Pb_3O_4 content. With increase in litharge content, the reactivity of the pigment with the organic vehicle increases. This produces an irreversible thickening and settling out, so that with high litharge content only short storage periods are possible. Conversely, the

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[5] Rock, G. H., *Trans. Soc. Nav. Arch. Mar. Eng.*, 39, 215 (1931).

[6] Jordan, L. A., and Whitby, L., "The Preservation of Iron and Steel by Means of Paint," p. 31, Sixteenth Bulletin, Paint Research Station, England.

97 per cent grade red lead is quite stable in its dispersion in a vehicle. The accepted opinion appears to be that a small quantity of litharge definitely adds beneficial properties to red lead. Its alkaline nature and its ability to form relatively insoluble soaps are credited for this beneficial action. Red lead is also believed to be inhibitive by virtue of its oxidizing nature.

The reactions of both red lead and litharge with the organic medium have been thoroughly studied[7, 8] and a number of intermediate reaction products with acidic and glycerol constituents in the drying oil have been isolated. Increasing the percentage of litharge decreases the moisture permeability and hardens the film. At the same time, it also causes an appreciable sacrifice in the chemical stability of red lead paint, carbonates, and perhaps other salts, being formed on exposure. The non-settling type of red lead, on the other hand, shows good stability on exposure.

As with all other pigments, a fine dispersion of pigment is essential. The particle size of most commercial red lead pigments ranges between 2 and 10 microns. Also, the pigment-vehicle ratio is important for obtaining best results, although inhibitive pigments, such as red lead, are not nearly as critical in their pigment-vehicle ratio as the more inert pigments. In general, a satisfactory priming coat using red lead should contain the maximum amount of well-dispersed pigment consistent with good brushing characteristics. The strong inhibitive character of red lead permits some reduction of the pigment with inert extenders without causing an excessive loss in protective quality. In Germany the incorporation of 20 to 40 per cent of barytes has become general practice. It is claimed[9] that the addition of this extender does not detract from the inhibitive qualities of the paint and indeed that it imparts beneficial application and film-forming properties. Reduction with other pigments, such as iron oxide or silicon carbide, has also been recommended.[9, 10]

White Lead

Basic carbonate white lead finds more use as a pigment ingredient in top coats than in priming coats. Its reactivity with the vehicle is definitely of a lower order in comparison with red lead. The same comments may be made with respect to sublimed blue lead; however, several investigators have reported good metal protection when these pigments were used in the priming coat.

Chromates

Two types of chromate pigments are being extensively used in priming paints. These are basic lead chromate and zinc chromate. For these

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[7] Ragg, M., *Farben Ztg.*, 34, 1605 (1929); *Trans. Electrochem. Soc.*, 64, 59 (1933).

[8] Gay, P. J., "Treatment of Linseed Oil with Litharge," Technical Paper No. 32, Paint Research Station, Teddington, England, 1932.

[9] Asser, E., *Farben-Ztg.*, 43, 553, 1938.

[10] Nelson, H. A., *Ind. Eng. Chem.*, 27, 40 (1937).

chromates to be effective as inhibitors, they must either be slightly alkaline, as in the case of basic lead chromate, or slightly soluble, as in the case of zinc chromate.[11] Basic lead chromate rated highest of a large number of pigments in a comparative series of tests conducted by the American Society for Testing Materials.[12] Zinc chromate, owing to its relatively high cost, is usually used in conjunction with other pigments, such as iron oxide, where it lends a definite inhibitive action to an otherwise inert pigment. It is finding increased use as a pigment component in protective priming coats over the more reactive metals, such as zinc, aluminum and magnesium, where red lead or the lead pigments are not suitable. The performance of the chromate pigments, particularly zinc chromate, is sensitive to acid environments. In highly industrial atmospheres, where appreciable quantities of SO_2 may be absorbed in the paint, the chromates, as previously mentioned, depolarize the cathodic hydrogen film, and thereby stimulate corrosion. Incorporation of a basic pigment with zinc chromate should aid in stabilizing the latter in acidic environments. However, in other atmospheres, the chromate pigments have given an excellent account of themselves.

Iron Oxide

Iron oxide pigments have been used in priming coats for many years. A number of iron oxides, both of natural and synthetic sources, are available. With the exception of the iron oxides containing calcium sulfate, they neither inhibit nor stimulate corrosion. Instead, these pigments form paint films of relatively high durability, retaining a high order of elasticity, and yet showing low water absorption.[13] For priming purposes, the practice of adding an inhibitive pigment to the iron oxide is increasing. In Germany,[14] the addition of 4 to 10 per cent of zinc oxide has become customary for the purpose of providing a red lead substitute. Another reinforcing pigment for the iron oxides is zinc chromate. In general, iron oxide pigments find more use as top coats than as primers. In the tests conducted by the British Iron and Steel Institute, iron oxide top coats over red lead primers have behaved very favorably.[15]

Micaceous iron ore (haematite) is finding wide use as a top coat material. The flaky structure of the mica component of this pigment has proved effective in reducing the permeation of moisture, without sacrificing acceptable appearance during exposure.

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[11] According to F. N. Speller, the solubility of zinc chromate in water is about 800 ppm., in paper on "Pretreatment of Metal Surfaces for Painting," presented at Am. Chem. Soc. meeting, March, 1938.

[12] *Proceedings American Society for Testing Materials*, 15, I, 220 (1915).

[13] Wilborn, F., Lōwa, A., Rossmann, E., Haug, R., *Farben-Ztg.*, 43, 57-9, 83-5, 106-8 (1938).

[14] Meier, E., *Farben-Ztg.*, 40, 616 (1935); Apel, *Farben-Ztg.*, 40, 590 (1935).

[15] Fourth Report of the Corrosion Committee, 1936, Iron and Steel Institute, London, England. Fifth Report of the Corrosion Committee, 1938, Iron and Steel Institute, London, England.

Zinc Pigments

Zinc oxide, owing to its basic character, imparts an inhibitive character to a priming coat. Owing to its relatively high reactivity, particularly with an acidic vehicle, it is customarily used in conjunction with other pigments, rather than by itself. When used in this manner, it increases both the tensile strength and the hardness of the coating. The reaction products with the vehicle are somewhat more water sorptive than those found with the lead pigments. A series of paints containing zinc oxide after 8 years' exposure gave on water immersion an absorption of between 15 to 30 per cent, whereas red lead paints showed between 3 and 7 per cent water absorption.[13]

Metallic zinc dust is also to be classed as an inhibitive type of pigment. The finely divided zinc powder is usually dispersed in the vehicle just before application. The vehicle should be of a low acid value to minimize hydrogen generation. The protective action of zinc dust is claimed to be due to the anodic character of the zinc metal with respect to iron. It is customary to add approximately 20 per cent of zinc oxide to the zinc dust paint to improve the application and film-forming characteristics. Another of the advantages of the paint lies in the fact that on aging, its color, namely battleship gray, is retained over long periods of time. Zinc-dust paint has been found to give particularly excellent service for use over zinc surfaces, such as galvanized iron. According to Nelson,[3] this may be attributed to the fact that the acidic component in the vehicle reacts preferentially with a more readily available zinc dust than with zinc at the base-metal interface.

Zinc sulphide and lithopone are not used as priming pigments. Their use is primarily restricted to top coats.

Aluminum [16]

Ordinarily the aluminum pigments are covered with an oxide film and very frequently with a film of organic polishing compound. This prevents the inherent anodic character of the aluminum metal from being utilized, except under conditions where a highly penetrative ion, such as a chloride ion, may penetrate through this surface coating. Consequently, for most exposures, aluminum pigments are extensively used in the top coats. Here a combination of several properties makes these pigments very useful. Aluminum pigments, owing to the method of manufacture, possess a lamellar structure. In addition, the particles are coated with an adherent organic film. As a result of this structure and surface condition the pigment particles have the property of laying themselves horizontally and concentrating in the outer part of the paint film. This "leafing" action serves to lengthen materially the path which moisture must traverse to get through the film, the metallic particles themselves being quite impermeable. In addition, the ability of the metallic pigment to exclude ultraviolet light is of a very high order. Each of these properties is fundamentally favorable to effective protection of the priming coat.

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[16] For a full discussion of the aluminum pigments, consult Edwards, J. D., "Aluminum Paint and Powder," 2nd ed., New York, Reinhold Publishing Corporation, 1936.

Several grades of aluminum powder are commercially available. They vary essentially in average particle size, and this in turn affects the appearance of the paint, the smaller particles making for a smoother and more satiny type of surface. Furthermore, the finer aluminum powders contain a larger number of particles per unit of weight, and hence are more effective in excluding moisture. The pigment, being essentially inert, shows a definite optimum pigment-vehicle ratio, and frequently a small reduction in the percentage of aluminum powder per gallon of paint brings about an appreciable reduction in protective quality. In this country, approximately two pounds of aluminum powder per gallon of vehicle is considered good practice for protective purposes. If an aluminum paste is used, somewhat smaller proportions of metallic aluminum are permissible, owing to the finer particle size used in pastes. Ordinarily 2 pounds of paste, containing about 65 per cent of metal, is used. For further decreasing the permeability of an aluminum coating, the use of a less permeable organic medium is definitely recommended, particularly in painting the more reactive metals, such as zinc, aluminum and magnesium.

Carbon Pigments

The lamellar structure of pigments has definite value, both as a means of increasing moisture impermeability and for the purpose of easing local mechanical stresses. Graphite pigments have shown good durability in top coats of steel protective paints. The use of graphite or other carbon pigments in priming coats is to be avoided owing to their tendency to stimulate corrosion. There are, of course, cases on record where paint systems in which graphite was used in priming coats have given a good account of themselves. In addition, the use of activated char, impregnated with NH_3, has been recommended as a priming pigment.[17] However, the consensus of opinion indicates that the use of ordinary carbon pigments should be confined to top coats.

Other Metallic Pigments

Several metals in a fine state of subdivision have been recommended for use as pigments in metal protective paints. The merit of such proposals, in general, lies in the fact that such pigments require a minimum amount of oil for suitable dispersion, and hence yield paint films which are composed largely of metal. Of these metallic pigments, the ones that have shown most promise are the metallic lead pigments. They usually consist of an alloy containing other metals in order to bring the electrochemical potential of the alloy very close to that of iron. Such a pigment, consisting of lead to which 13 per cent antimony and 2 per cent tin has been added, has been patented. Paints with this pigment have been compared with red lead as a primer by the British Paint Research Station,[6] and have been proved to give excellent service, particularly in several corrosive environments. These pigments are relatively inert toward the vehicle, but, owing to their high specific gravity, they tend to settle rather quickly and for this reason require good stirring before application.

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[17] Rossmann, E., *Farbe u. Lack*, 53-4, 68, 78 (1937).

EVALUATION OF PRIMING PIGMENTS

Owing to the long life which a good paint system shows on atmospheric exposure, various attempts have been made to evaluate the suitability of priming pigments in a more rapid fashion. True enough, exposure tests with suitable paints are essential to furnish the necessary background against which the validity of the more rapid tests on pigments can be established. Even though within the past 25 years a number of important exposure tests have been conducted, some of which are still incomplete, unanimity of opinion with regard to the relative merit of a number of pigments with respect to their corrosion protective value has not as yet been reached. Weighing the various findings of different investigators, the classification shown in Table 30 may be considered as an average opinion.

Table 30.—Classification of Priming Pigments.

Inhibitors	Indeterminates	Stimulators
Red lead	White lead	Certain iron oxides
Red lead+Litharge	Certain iron oxides	Extenders:
Zinc dust	Aluminum	Whiting
Zinc oxide	Chrome oxide	Blanc fixe
Lead alloy	Lead titanate	Lampblack
Ammoniated char (?)	Silica	Graphite
Sublimed blue lead	Barytes	
Zinc chromate	Lead chromate	
Basic lead chromate		

In an effort to reduce the time required by exposure tests, several short-cut methods have been proposed as a means of examining the inhibitive character of various pigments. A simple scratch test has been developed which has found wide use.[18] In this test, a drop of .001M sodium chloride is placed on a carefully made scratch through a dried paint coating and the effect of this dilute solution on the scratched section of the test panel is noted. Inhibitive pigments prevent both rust formation and paint softening. The results are summarized in Table 31.

In order to get more quantitative evidence regarding relative inhibitive character of pigments, the same workers carried out a careful series of tests in which metal, pigment and distilled water or several dilute electrolytes were rotated in sealed tubes for 20-hour periods. At the end of this period, the loss in weight of the metal specimen was determined.

More recently,[19] a technique has been developed whereby with the aid of a vacuum tube electrometer, time-potential curves are obtained and the

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[18] Lewis, K. G., and Evans, U. R., *J. Soc. Chem. Ind.*, **53**, 29T (1934).

[19] Burns, R. M., and Haring, H. E., *Trans. Electrochem. Soc.*, **69**, 169 (1936).

Table 31.—Behavior of Pigments in the Scratched-Coat Test with 0.001*M* Sodium Chloride.[18]

Definite Inhibition. (No corrosion at the scratch)

- Litharge (2 varieties)
- Red lead (3 varieties)
- Zinc oxide* (4 varieties)
- Zinc dust
- Blom alloy pigment

Definite Corrosion at Scratch

- Iron oxide (7 varieties)
- Lead oxalate
- Lead sulphate
- White lead
- Lead chromate (2 varieties)
- Barium sulphate (2 varieties)
- Graphite
- Lampblack

Doubtful Inhibition

- Lead peroxide
- Manganese dioxide
- Magnesium oxide (2 varieties)
- Magnesium basic carbonate

Definite Corrosion at Scratch

- Aluminum (2 varieties)
- Arsenious oxide (2 varieties)
- Antimonious oxide
- Stannic oxide
- Titanic oxide
- Emery flour
- Silicon carbide

* Zinc oxide must be distinguished from *lithopone* (co-deposited zinc sulphide and barium sulphate). This gave much less favorable results than zinc oxide in the tests of E. Maass and R. Kempf, *Korr. Met.*, 3, 131 (1927), possibly as a result of the sulphide content.

corrosion behavior of painted iron specimens directly followed. These studies have shown that iron oxide in a paint protects essentially by mechanical exclusion of corrosive agents, whereas red lead shows positive inhibitive properties. This work has since been greatly extended to include a large number of pigments and several different vehicles.[19a]

In these recent investigations 25 representative single pigments and several combinations of these were incorporated, 25 per cent by volume, in a varnish-reinforced linseed oil vehicle. A 25 per cent by volume pigment-vehicle ratio was arbitrarily selected in lieu of determining the optimum pigment-vehicle ratio for each pigment. The composition of the vehicle was as follows:

Ingredient	Per cent by weight
Raw linseed oil	66.7
Bodied linseed oil	11.1
Varnish (100% phenolic resin, 25 gallon oil length, the oil consisting of 90% Chinawood oil and 10% bodied linseed oil)	22.2 + necessary drier
Lead	about 1 per cent on oil basis
Cobalt	0.1 per cent on oil basis

In addition to this vehicle, some comparative tests were also made with a straight linseed oil vehicle and another vehicle consisting of a phenol-modified and oil-extended alkyd resin in suitable solvents. The coating materials were weighed out, mixed, and brushed to approximately 0.001-inch thickness over carefully cleaned low-carbon steel panels. Cleaning consisted of rubbing with alumina, followed by a wash in distilled water and finally in purified acetone. The coated panels were allowed to dry at 25° C., and 50 per cent relative humidity one week between coats and several weeks prior to outdoor exposure.

[19a] Haring, H. E., Gibney, R. B., and Clarke, W. I. Shortly to be published.

In Figure 64 are shown the time-potential curves of a number of single-pigment paints which had been exposed three months indoors at 25° C., and 50 per cent relative humidity. A probe electrode, consisting of a glass tube filled with tap water, was connected by means of a salt bridge to a calomel half-cell, which in turn was connected through a potentiometer circuit to the bare steel underside of the panel. In order to avoid complicating cathode reactions due to oxygen absorption, the contacting electrode was bathed in an atmosphere of nitrogen.

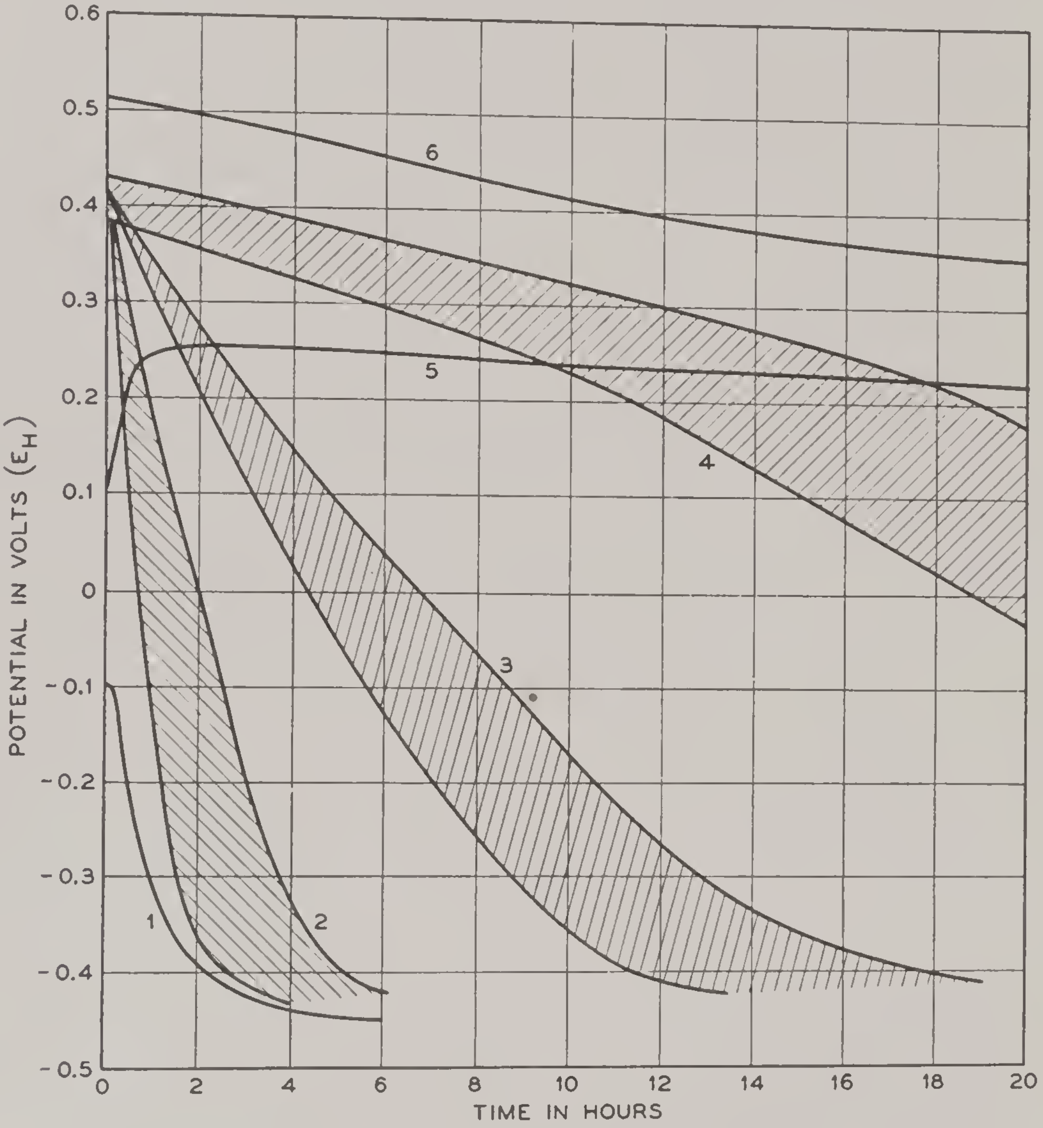

Figure 64.—Time-Potential Curves for Various Pigments in Common Vehicle. Panels Aged Three Months Indoors (25° C.-50% Relative Humidity).

1—Bare Steel Panel.
2—Unpigmented Coating, Following Pigments, 25% by Volume: Silica, Magnetic Iron Oxide, Graphite, Several Iron Oxides, Cadmium Red, Whiting.
3—Iron Oxide, Basic Lead Chromate, Lead Titanate, Aluminum Powder.
4—Zinc Chromate, Zinc Oxide, Zinc Dust.
5—Red Lead (97% Grade).
6—B.C. White Lead, Sublimed Blue Lead. Resin-Reinforced Linseed Oil.

It will be recalled from the discussion in Chapter 1 of the potential of passive and active iron surfaces and the trend of time-potential curves, as illustrated in Figure 6, that electropositive potentials are associated with passivity and electronegative potentials with corroding action. In the light of this behavior, it is of interest to examine the results of the recent study given in Figure 64. The time-potential behavior of these pigments may be represented by distinct classes. As a means of simplification, these classes have been purposely separated, although actually many borderline cases were found. It will be remembered that such a classification does not by itself permit evaluation of a given paint for purposes of corrosion protection, but instead merely indicates the inherent relative inhibiting tendencies of various pigments.

As may be seen from Figure 65, outdoor aging for a period of 9 months

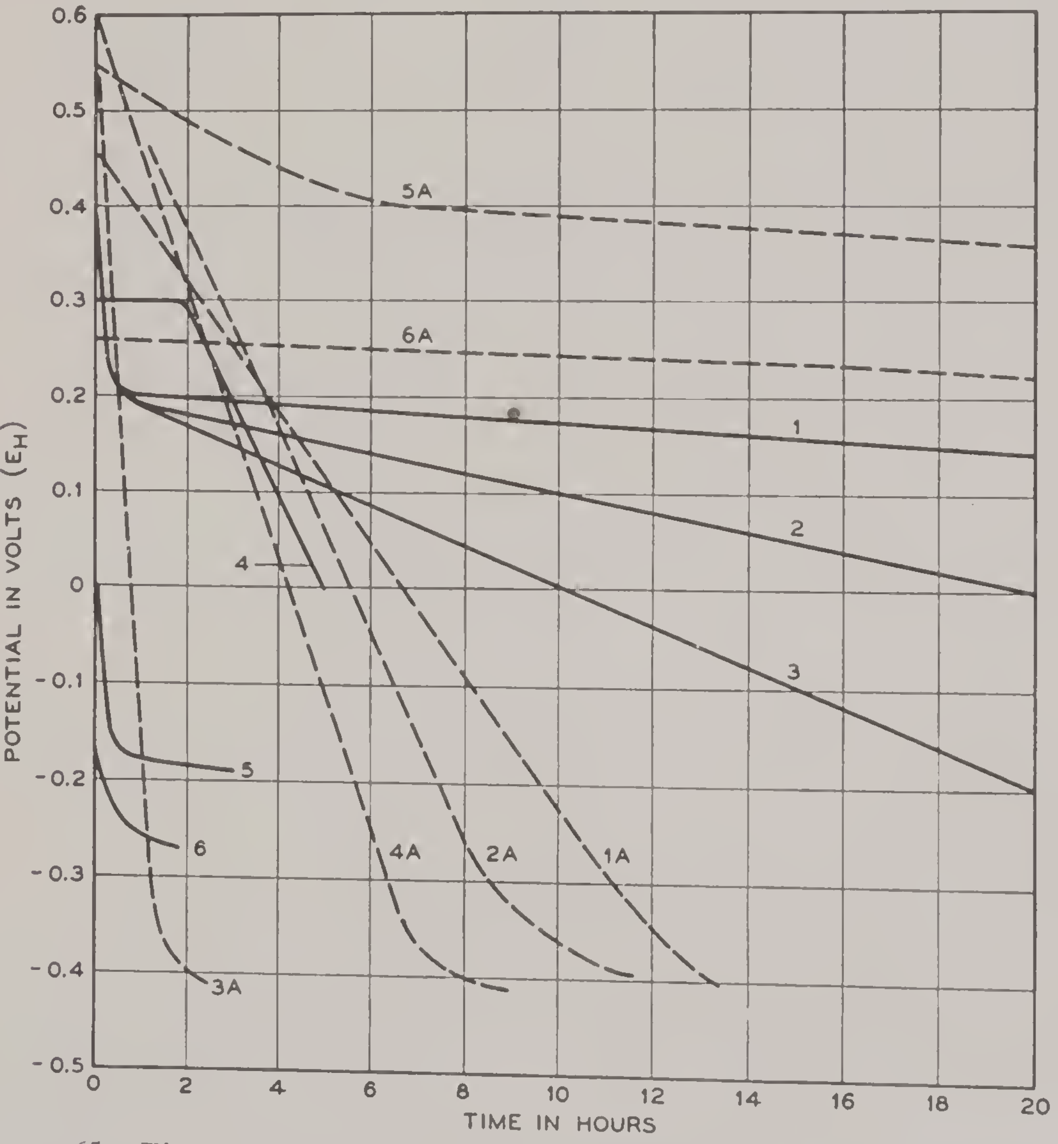

Figure 65.—Time-Potential Curves Showing Effect of Aging on Various Pigments in a Common Vehicle. Dashed Curves for Panels Aged Three Months Indoors (25° C.-50% Relative Humidity); Solid Curves for Panels Aged Nine Months on Roof (Summit, N. J.).

1—Basic Lead Chromate.
2—Lead Titanate.
3—Chrome Oxide.
4—Iron Oxide.
5—B.C. White Lead.
6—Zinc Oxide.
Vehicle, Reinforced Linseed Oil.

(exposure tests begun in February) has definitely altered the position of the time-potential curves of a number of the paints. Thus, paints made up of the single pigments zinc oxide or white lead have definitely lost protective properties as a result of 9 months' outdoor exposure, owing to attack of the binding medium by exposure factors. As might be expected, the zinc oxide paint showed deep cracks to the base metal and the shift of the

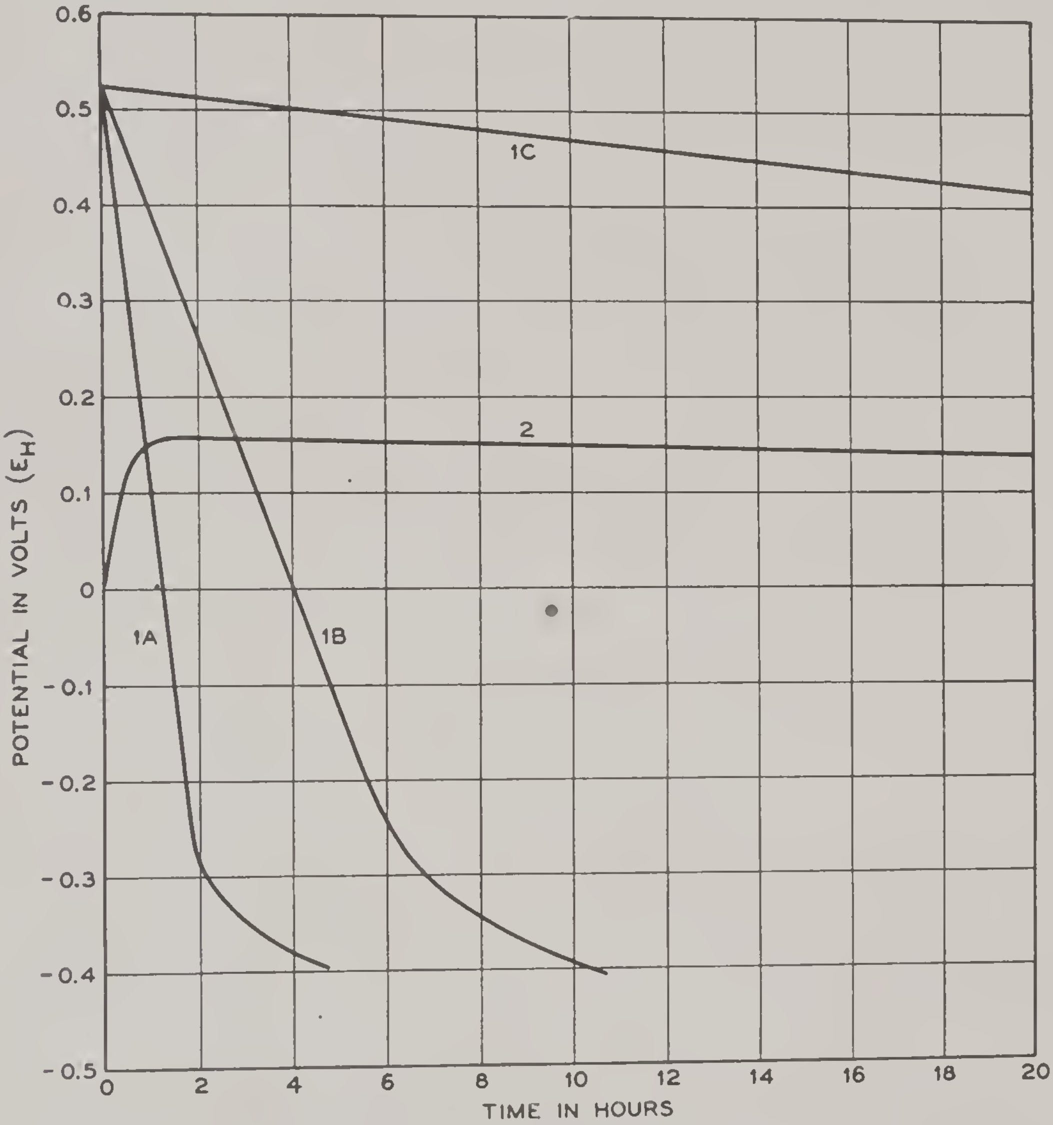

Figure 66.—Time-Potential Curves Showing Effect of Vehicle. Panels Aged Three Months Indoors (25° C.-50% Relative Humidity).

1A—Iron Oxide or Iron Oxide-Basic Lead Chromate 2:1 in Linseed Oil.
1B—Same in Varnish-Reinforced Linseed Oil.
1C—Same in Phenolic Alkyd Resin Vehicle.
2—Red Lead in Linseed Oil or Reinforced Oil.

white lead paint may possibly be attributable to the degradation of the vehicle, probably owing to the poor ultraviolet light exclusion of this pigment. It must be borne in mind that paints made of these pigments alone would find use for priming purposes only and would in practice be followed by suitable top coats. On the other hand, paints made up of the single pigments, basic lead chromate, lead titanate, and chrome oxide, have definitely improved on exposure in their ability to delay corrosion. The iron oxide paint also has shown no loss in protective properties. These pigments are definitely of the non-reactive type and also have good ultraviolet light exclusion properties. With basic lead chromate, the weakly basic character of the pigment appears to have struck an effective compromise between anodic protection due to alkalinity and moderate reactivity with the vehicle.

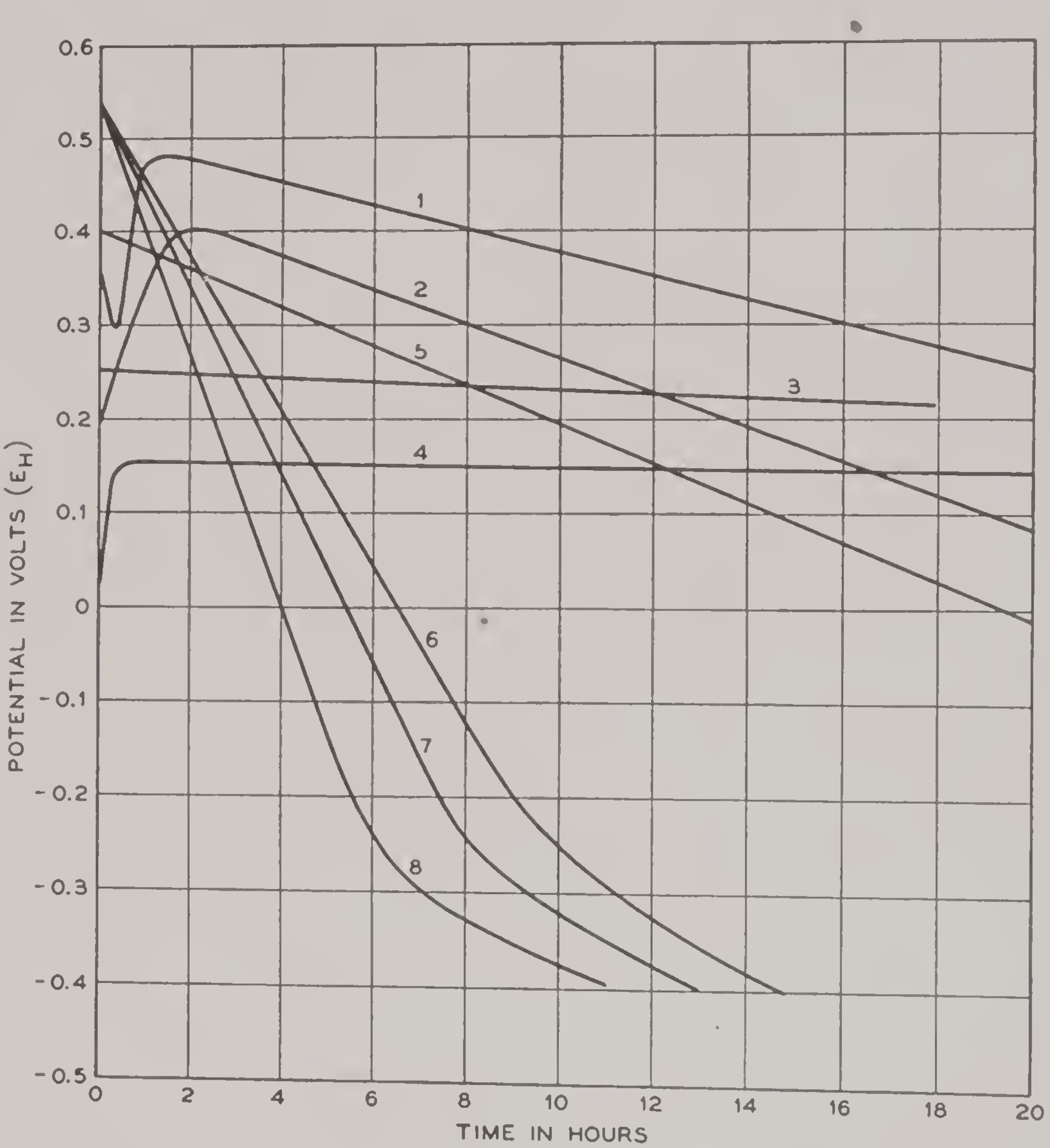

Figure 67.—Time-Potential Curves Showing Effect of Mixed Pigments in a Common Vehicle. Panels Aged Three Months Indoors (25° C.-50% Relative Humidity).

1—Zinc Dust-Zinc Oxide, 4:1.
2—Zinc Dust.
3—Zinc Oxide.
4—Red Lead Alone; Red Lead-Basic Lead Chromate, 2:1.
5—Zinc Chromate; Iron Oxide Zinc Chromate, 2:1.
6—Basic Lead Chromate.
7—Iron Oxide-Basic Lead Chromate, 2:1.
8—Iron Oxide.
Vehicle, Reinforced Linseed Oil.

Most of these paints give time-potential curves which incline at various angles toward the corrosive potential zone, namely, a negative potential −0.2 to −0.4 volt. Red lead and zinc dust are the only two pigments in this series which show a change towards a positive potential soon after wetting by the electrode. The chief difference in the remaining pigments lies in the steepness of their slopes to the corrosive potential zone, and it may well be that this is of practical significance in characterizing a protective and non-protective pigment. Undoubtedly, the ease with which moisture can reach the metallic base affects the slope of these time-potential curves. This is shown to be the case in Figure 66, where several single and mixed pigments were dispersed in different vehicles, namely, linseed oil, varnish-reinforced linseed oil and the phenolic alkyd vehicle. Of these vehicles, linseed oil yields the most permeable film and the phenolic alkyd resin vehicle the least. The pigments dispersed in linseed oil give a steep slope and those dispersed in the resin vehicle show a very slow change in potential. It can also be seen that when a strongly inhibitive pigment, such as red lead, is used, the difference in vehicle has practically no effect on the position of the time-potential curves.

The effect of mixed pigments is shown in Figure 67. The combination of 4 parts zinc dust and 1 part zinc oxide is shown to be better than either of the pigments alone. Addition of zinc chromate (1 part) to iron oxide (2 parts) brings the time-potential curve to that of the zinc chromate alone, indicating a controlling effect due to the zinc chromate pigment. In a mixture of lead chromate and iron oxide, on the other hand, the time-potential curve lies approximately midway between curves of the two single pigments. Again, red lead is found to be dominant in its behavior, being insensitive to the presence of other pigments. With the exception of the curves shown in Figure 65, all the other time-potential curves were taken after an exposure of three months indoors.

This time-potential method of characterizing pigments illustrates a point made previously, namely, that any single test method may have definite value in elucidating one of the mechanisms determining paint durability, yet by itself is insufficient to permit complete prognostication of the serviceability of a given paint coating. Other factors, such as permeability to moisture and gases, reactivity of the vehicle with the base metal, ultraviolet light exclusion, physical structure of the coating, etc., may exert a preponderating influence on the overall behavior of a particular paint.

ADHESION

Any paint, regardless of the purpose it serves, must adhere well for relatively long periods of time to the underlying base material. Hence a consideration of the factors that determine and influence adherence will contribute to an understanding of the durability of paints. As a rule, evidence of poor adherence, such as flaking, peeling, easy removal by some external force, etc., are so glaringly conspicuous as to suggest a simple cause for the loss of adherence. Actually, however, these final signs of loss of adherence are usually the net effect of a prolonged tug-of-war among a large number of competing forces. Although the final evidence of poor adherence may be the same for several different kinds of coatings, the causes and the course of failure for each may be quite different.

Initial Adhesion

Provided reasonable care is exercised in the application of a paint to a metal, it should not be difficult to obtain a high order of initial adherence. The primary requirement is that the paint medium come into direct contact with the base metal. If this is made possible, the electrical forces residing in the atoms and molecules of the metal surface can readily interact with the electrical forces residing in the polar molecules of the finishing medium. The distance over which these attractive forces can act is extremely short, being at most of the order of several molecular layers of the constituents in the coating medium. Their sphere of influence drops to a negligible quantity at distances of the order of a few hundred Angstrom units from the substrate surface, and such a distance comprises only about one-thousandth of the thickness of an average single-coat paint film. For this reason, the critical study of the metallic substrate structure requires the use of refined tools, such as the electron diffraction beam, for characterization of the metal surfaces. Actually it is known that true metallic surfaces are probably never presented to a paint medium, since most metals are covered with thin layers of surface compounds, such as oxides, sulfides, carbonates, etc.

Every organic coating material, whether oil, paint, varnish or lacquer, consists of a complex mixture of diverse kinds, sizes and shapes of molecules. This heterogeneity is essential for proper film-forming characteristics. These mixtures contain molecules or molecular groups which are varyingly asymmetrical and thus have varied fields of force along their molecular surfaces. It is this variation in molecular architecture of both the substrate surface and the paint medium which provides the source of bonding forces and the resultant tendencies to develop adhesion. The molecules or atoms in the substrate surface are fixed in space and hence, in order to make alignment of these electrical forces possible, a certain degree of mobility of the adhesive constituents in the organic medium must be provided. This is usually accomplished by the use of solvents, heat, or a combination of these. In the case of drying oil films, the linseed oil itself at the time of application offers sufficient mobility to permit the desired orientation for developing adhesion.

Although these short-range forces are fundamental to the development of adhesion, in actual paint practice a number of other factors of more gross nature control the initial adherence.

Physical and Chemical State of the Metal Surface

Both the physical texture of a surface and its state of cleanliness are obviously important in obtaining good initial adherence. In paint technology, it is well-recognized that highly polished surfaces offer more difficulty than mechanically roughened surfaces. One obvious reason for this difference is the fact that roughened surfaces provide more actual surface area per unit of macroscopic area. The measurement of true surface area of a solid offers a real technical difficulty. One method of roughly approxi-

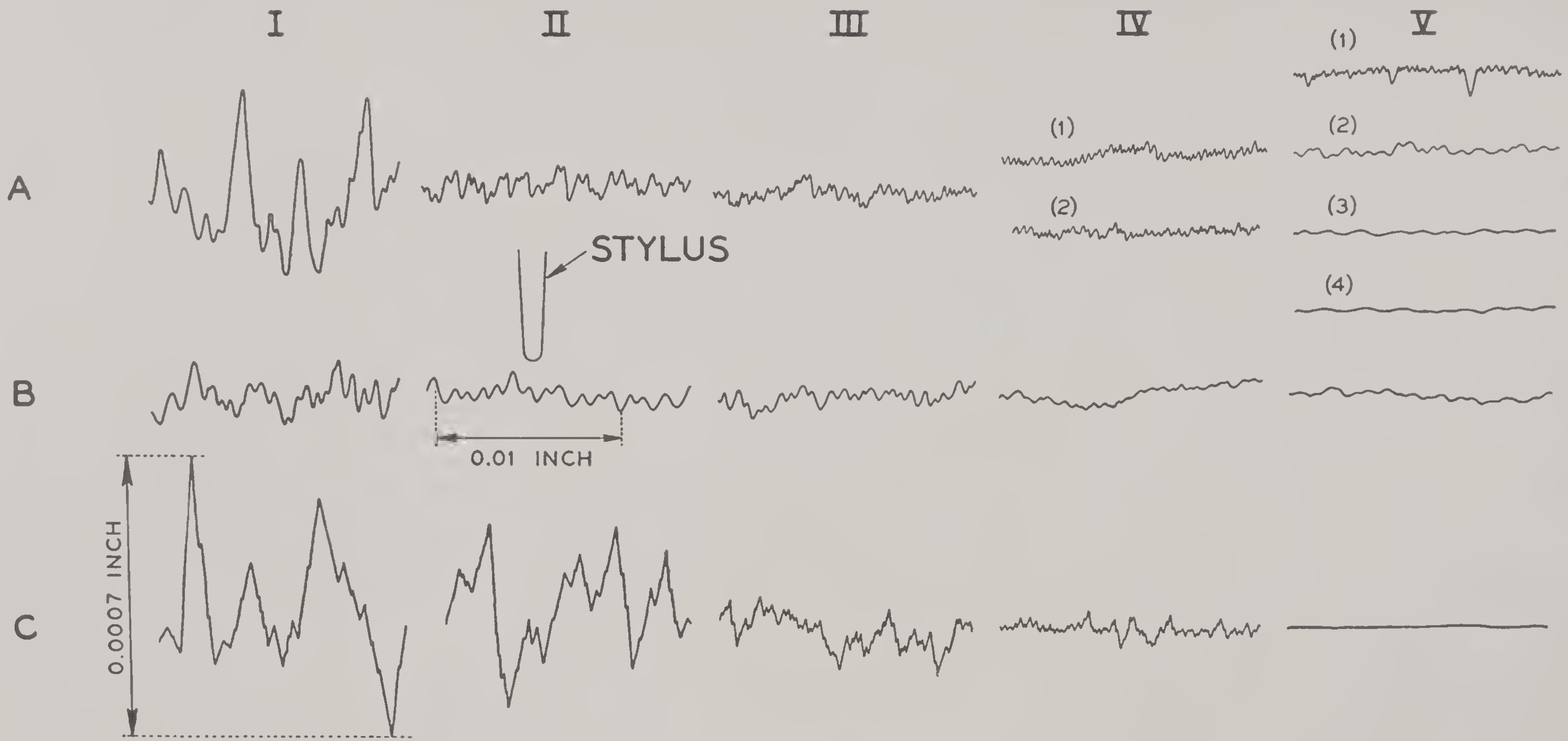

Figure 68.—Surface Contour of Various Roughened Solids.

Magnification: Vertical: 4700; Horizontal: 210. Radius of Stylus: 0.0005 inch.

Materials: A—Steel, brass, aluminum, phenol fibre.
B—Hard rubber.
C—Glass.

Treatments: I— 60-mesh steel grit—30 pounds air pressure.
II—100-mesh silicon carbide—30 pounds air pressure.
III—180-mesh silicon carbide—30 pounds air pressure.
IV—400-mesh silicon carbide—30 pounds air pressure.
(1) Steel and phenol fibre; (2) brass and aluminum.
V—As received.
(1) Cold-rolled steel; (2) brass; (3) aluminum; (4) phenol fibre.

mating the increase in surface area by mechanical roughening consists of measuring the surface contour by means of a finely pointed diamond stylus, the horizontal and vertical motions of which, as it passes over the surface, are amplified to a high degree. Figure 68 illustrates the surface contour of several solids roughened by the use of abrasives of different particle size. A minimum surface area increase of twentyfold is indicated in several instances. As previously stated, such a method at best can give only an approximation of true surface contour, inasmuch as the finite sharpness of the stylus point limits the extent to which the contour can be followed. For instance, tracings obtained on polished aluminum and on the same metal surface after it had been anodically oxidized gave indistinguishable tracings. It is known, however, that the anodic oxide coating has a fine pore structure and this was evidently too fine for the stylus to penetrate. According to Rummel,[20] the cross-section of such pores is estimated to be 10^{-5} centimeter and the spacing between pores 10^{-4} centimeter. With a depth of oxide coating of 10^{-3}, the estimated surface increase would be approximately $12\frac{1}{2}$ times the original surface area. Although the contour tracings of these two surfaces were identical, adhesional strength measurements with organic coatings have shown a definite increase in joint strength after anodic oxidation, thus indicating that organic coatings do penetrate into these pores.

The irregular contour produced by mechanical roughening methods, such as blasting, is made up of many tiny facets inclined to each other at various angles, which condition probably aids in keying in the organic finish to the surface by neutralizing stresses normal to it. However, it is quite possible that the major benefit obtained by these mechanical roughening methods is attributable to the removal of foreign contaminating elements, producing thereby a very clean surface. It is a known fact that immediately after blasting, a metal specimen will be completely wetted by water. Short exposures to ordinary indoor air for a matter of only a few minutes destroys this property of complete wetting. This illustrates the desirability of minimizing the time between any surface cleaning operation and the application of an organic coating.

In practice, practically all metals to which a coat of paint is to be applied are covered with various macroscopic films, usually thousands of molecular layers in thickness. Such layers may be composed of rust, mill scale, other surface compounds, hydrates, dirt, greases, etc. The problem for the paint technologist, therefore, lies in cleaning and homogenizing the surface, as well as is economically feasible, and the importance of such cleaning is well recognized. Whereas a contaminated layer may itself be readily wetted by a paint vehicle, its own cohesive strength or its adhesion to the base metal is frequently of a low order, and hence the adhesion of the paint film to the metal is low. Thus, by lack of cleanliness, a weak link is forged into what otherwise might have been a strong chain.

[20] Rummel, T., *Z. Physik*, **99**, 518-551 (1936).

Some recent experiments have indicated that a contamination by grease or oil to the extent of a few tenths of a milligram of contaminant per square inch of metal surface definitely affects the adherence of most organic finishes. This amount of contaminant represents an appreciable number of molecular layers. From an engineering point of view, this points to the need of a high order of cleanliness. Undoubtedly, the degree of compatibility of the organic contaminant with the finishing medium plays an important part. It is a well known fact that a number of the modern synthetic baking type of finishes, owing to a more restricted compatibility with oils and greases, are more sensitive to surface contaminations than the older type of oleoresinous baking finishes.

In further recent studies of adhesives,* several thermoplastic resins, *e.g.*, polystyrene, ethyl cellulose, and polyvinyl acetate, were examined for the effect of various organic contaminants on the strength of joint obtainable against a thoroughly cleaned and polished metal surface. The contaminants, two per cent by weight, were dispersed in the resins on hot differential-speed rolls, and the technique of assembling the thermoplastic joint was maintained constant. In the following table are shown in pounds per square inch the joint strengths in tension obtained:

Table 32.—Joint Strength of Various Thermoplastic Resins.

(Pounds per square inch)

		Polystyrene	Ethyl Cellulose	Polyvinyl Acetate
Unmodified		3000	2250	5800
Dibutyl phthalate	2%	3000	2250	5800
Paraffin	2%	2000	2700	3700
Cetyl alcohol	2%	<100	1100	2150
n-Butyl stearate	2%	230	750	1750
Stearic acid	2%	<100	<100	100

It can be seen that a compatible material, such as dibutyl phthalate, has little effect on the joint strength of these resins. The contrast between the non-polar paraffin and the highly polar asymmetrical stearic acid is of particular interest. These two materials were examined in greater detail for their effect on joint strengths of polystyrene. It was found that paraffin could be incorporated to as much as ten per cent by weight of the resin, the strength of the bond being reduced only from 3000 pounds per square inch to about 1800 pounds. Stearic acid, on the other hand, caused a complete loss of adhesion when admixed in very small proportions. An addition of 0.001 per cent showed no drop in joint strength, but when 0.1 per cent was added, a level of less than 100 pounds was obtained. When such a weak joint was broken, the metal surfaces appeared clean, both to the eye and under the microscope. However, the electron diffraction beam † revealed a pattern attributable to a mixture of stearic acid and polystyrene and the layer adhering to the metal was estimated to be about 85Å thick. Rubbing with clean rice paper revealed a layer next to the metal surface about 25Å in thickness having the pure pattern of well oriented stearic acid.

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* Studies conducted by Messrs. W. J. Clarke and J. B. DeCoste of the Bell Telephone Laboratories, New York.

† The electron diffraction beam patterns were obtained and interpreted by Messrs. L. H. Germer and K. H. Storks of the Bell Telephone Laboratories, New York.

There is need for considerably more study to obtain a better understanding with regard to the effect of a number of specific organic contaminants and different finishing media.

A number of practical methods are in use for removal of organic contaminants. For immobile outdoor structures, a final generous wiping with rags saturated with volatile organic solvents is frequently employed. For indoor equipment, the practice of degreasing by the condensation of solvent vapors is becoming of increasing importance. For this purpose, noninflammable solvents, such as trichlorethylene, are most generally used.[21]

Suitable equipment has recently been developed in which metallic parts of various sizes and shapes can be effectively and expeditiously degreased. The feature of condensation of clean solvent vapors on the work to be degreased marks a definite step forward over the older methods, where the solvent in which work had to be immersed became increasingly contaminated. The high specific gravity of the trichlorethylene vapors reduces solvent loss to a minimum, owing to the ease with which the vapors can be confined within a desired space. The details of this method of degreasing are fully discussed in Chapter 2. The order of cleanliness obtained is in general adequate for the development of a high order of adhesion for most organic finishes.

Inorganic Contaminants

The removal of inorganic contaminants, such as rust, scale, etc., is an old problem. It is now rather generally agreed that on steel the removal of rust and scale are necessary if long paint life is to be expected. Rust, being of a sorptive open structure, is usually contaminated with salts of various kinds, which can exert an osmotic effect on the water permeating through a paint film and accelerate progressive corrosion beneath the paint. Whereas clean ferric hydroxide may not be injurious, in practice such a pure hydroxide is probably never encountered, and hence best practice dictates complete removal of rust, if economically possible. Mill scale varies in its tenacity of adherence to the base metal. It sets up a definite electrochemical potential with respect to iron, so that at all points or lines, where there is discontinuity between the scale and the metal underneath, an increased opportunity for corrosion is developed. Another difficulty associated with mill scale is its brittle character which makes it sensitive to splitting or cracking as a result of impact. A well adhering and continuous scale would offer considerable protection and would be a satisfactory base upon which to paint. However, it is difficult at any time to be assured of such a continuous scale. Partial removal of scale is probably worse from the standpoint of corrosion of painted iron than either no removal or complete removal. The effect of surface condition on the durability of various paints, as judged by exposure tests, is illustrated in Table 33.[22] Surface cleaning appears to outweigh in importance the composition of the several paints investigated. None of the paints failed after 5.6 years when the scale had been completely removed by pickling, whereas the majority failed in a relatively short time when the scale had been only partially removed as by weathering prior to painting. The commercial pretreatment of steel to be painted and exposed to the atmosphere will be discussed in greater detail in Chapter 15.

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[21] Davidson, W. W., *Trans. Electrochem. Soc.*, 72, 413 (1937).

Table 33.—Effect of Surface Condition (Up to 5.6 Years' Exposure).

	Life in Years[1]					
					Means	
Paint	1 Pickled	2 Weathered	3 Weathered and Heated	4 Weathered, Washed and Heated	Cols. 1-3	Cols. 1-4
Lead chromate	>5.6	2.7	>5.6	...	>4.6	...
Red oxide+zinc chromate	>5.6	3.7	5.3	>5.6	>4.9	>5.1
Red oxide	>5.6	1.8	2.8[2]	2.2	>3.4	>3.1
Black bitumen	>5.6	2.6[2]	2.2[2]	...	>3.5	...
Micaceous iron ore	>5.6	0.6	0.6	1.1	>2.3	>2.0
White lead	>5.6	2.2	1.7	2.7	>3.2	>3.1
Red lead	>5.6	1.1	>5.6	...	>4.1	...
Means of 7	>5.6	2.1	>3.4	...		
Means of 4	>5.6	2.1	2.6	>2.9		

[1] Time of exposure up to which the average grading of the front and back of the specimens was 3 or less.

[2] In the case of these specimens failure was not reported at two consecutive inspections and mean values have, therefore, been assessed for the lives.

Another manner in which the chemical nature of a metal may influence the adherence of organic finishes is by the chemical reactions which a more active base metal can undergo with reactive components in the finish vehicle. With the wide adoption of new die-cast alloys of such metals as zinc, aluminum and magnesium, this is assuming increasing importance. It is quite likely that the initial adherence of organic coatings to clean surfaces of these metals is as high as that obtained with less reactive metals. However, the penetration of small quantities of moisture through the paint film to the metal surface causes difficulties of retaining adherence. In order to minimize this, it has become the practice to subject these metals to chemical treatments of various kinds, whereby the metal surface becomes converted to an adherent chemically inert compound.

In the case of iron and steel, wherever feasible the practice of converting the iron to an insoluble phosphate surface is becoming increasingly adopted. The method is obviously restricted to structures which can be brought to the point of treatment. However, it is interesting to note that even in the field of large structures, phosphating treatments have been recommended. Thus, for painting iron structures, the removal of rust or old paint, followed by a brush application of 33-per cent aqueous solution of phosphoric acid, has been recommended.[23] This is then followed on the next day with a wash of a milk of lime suspension to neutralize unreacted acid, after which the customary application of a suitable paint system takes place. Smaller work which can be transported to the site of the process installation is converted to a crystalline phosphate surface by various chemical processes now in wide use. The details of such processes are discussed in Chapter 16. These phosphate coatings by themselves are not adequate in their rust protective quality for prolonged outdoor exposure. They do, however, provide an excellent base for the adherence of paint coatings and serve effectively to minimize lateral propagation of rust at scratches through the coatings.

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[22] Hudson, J. C., Fifth Report of the Corrosion Committee, Iron and Steel Inst., p. 267, London, 1938.

In order to improve the adhesion of organic finishes to zinc, phosphating treatments, similar to those used on steel, are coming into use. For many years, considerable difficulty has been experienced with the painting of galvanized iron. Ordinarily hot-galvanizing produces a smooth and broadly crystalline structure of the zinc surface which, on emersion from the hot-galvanizing tank, becomes covered with a surface layer of a fatty material, such as palm oil, and with acidic flux components. Hence it is necessary to clean the surface thoroughly to obtain good adhesion. A number of methods for accomplishing this have been recommended. One is to permit galvanized iron structures to be exposed for a period of at least 6 months before painting. Other methods consist of mechanical roughening, treatment with solvents to remove grease, the use of various etching solutions, and treatment with metallic solutions which deposit a metallic layer on the zinc. Certain primers carrying a high percentage of zinc dust have been found effective.[24]

One of the important factors making for poor adherence of paints over reactive metals is concerned with certain chemical reactions occurring in the paint film itself. During the early stage of drying of a linseed oil film, where oxidation is the predominant mechanism, a number of reactive decomposition products are generated. These, particularly in the presence of moisture, are given an opportunity to react with the metal at the interface. Among the decomposition products have been identified[25] such organic acids as formic, propionic, caproic, pelargonic, azelaic, and other higher acids, both saturated and unsaturated. In addition to these, acetic acid, aldehydes, carbon monoxide, carbon dioxide, hydrogen peroxide, etc., have been reported.[26] Zinc formate has been isolated at the interface between paint and the metal surface[26] and the formation of formic acid has been suggested as one of the possible causes for low adherence of paints to zinc surfaces. Unquestionably the exposure conditions during the early life of a paint film influence the degree to which such reactive constituents can form and react with the base metal. It was found, for instance,[27] that certain varnish enamels, when applied to brass, lost their adhesion within two months of outdoor exposure, whereas the same materials, when exposed indoors at a controlled humidity of 50 per cent, had not lost adhesion after several years.

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[23] Peters, H. A. J., *Verfkroniek*, 10, 124 (1937).

[24] Duncan, D. R., "Technical Paper No. 62," The Research Association of British Paint, Color and Varnish Manufacturers, January, 1935; Nelson, H. A., and Kittelberger, W. W., *Ind. Eng. Chem.*, 25, 27 (1933); Jordan, L. A., *Chem. and Ind.*, 56, 361 (1937); Nelson, H. A., *Ind. Eng. Chem.*, 27, 1449 (1935).

[25] Merzbacher, *Chem. Umschau Fette, Ole, Wachse, Harze*, 36, 339 (1929); Eibner, A., "Das Oltrocknen ein kolloider Vorgang aus chemischen Ursachen," p. 143, *Allg. Industrie-Verlag*, 1931.

[26] Wing, H. J., *Ind. Eng. Chem.*, 28, 292 (1936).

Aluminum and its alloys when exposed in severe environments suffer loss of adherence. There is some difference between the various aluminum alloys in this respect, those containing magnesium behaving less favorably than the others.[28] In order to obtain the maximum order of adherence on aluminum, the use of electrolytically produced oxide coatings as a base for the paint has proved very effective. The methods of producing these coatings are described in Chapter 16. Such coatings are usually a few ten-thousandths of an inch in thickness; and their columnar structure, as well as the presence of many fine pores, provide an excellent opportunity for the anchorage of a paint film. For those cases where an anodic oxide coating cannot be applied, a thorough cleaning followed by a wash in dichromate has proved effective. For outdoor structures, the use of an inhibitive pigment is definitely recommended. The incorporation of zinc chromate in a relatively non-permeable vehicle, such as a phenolic varnish, has given excellent service. Paints pigmented with zinc oxide have been found particularly suitable for protecting aluminum or its alloys used in warship construction against attack by sea-water.[29]

Magnesium and its alloys offers still more difficulty in obtaining a high order of adherence, owing to the high reactivity of this metal. Here also, surface conversion treatments have been found effective for promoting adherence. A short immersion in a solution containing sodium dichromate and nitric acid has been found effective for this purpose.[30] This treatment requires a dip of only one minute and produces a film well suited for the adherence of paints. In addition, chemical conversion to selenides[31] and electrolytically produced fluorides[32] has been recommended for the production of surfaces suitable for painting. Again, the selection of suitable priming pigments is important, and the use of a paint medium containing zinc chromate in a tung oil-phenolic resin varnish vehicle has been found the best.

Whereas it is obviously important to obtain a high order of initial adherence of a paint coating, from the standpoint of durability the retention of adherence is really more important. Adherence retention is dependent on several factors, one of which is the nature of the primer. With a truly inhibitive pigment in a primer, the effect of moisture permeating through the coating is not as serious as in those cases where an indifferent or corrosion stimulating pigment is used. Nevertheless, it is highly desirable to minimize, as far as possible, the amount of moisture that may penetrate to the base metal.

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[27] Schuh, A. E., and Theuerer, H. C., *Ind. Eng. Chem.*, 29, 182 (1937).

[28] Edwards, J. D., and Wray, R. I., *Ind. Eng. Chem.*, 27, 1145 (1935).

[29] Ulffers, *Farben Ztg.*, 42, 235 (1937).

[30] Winston, A. W., Reed, J. B., and Gross, W. H., *Ind. Eng. Chem.*, 27, 1333 (1935).

[31] Bengough, G. D., British Patent 378,916.

[32] Fischer, H., and Schwan, W., *Wiss. Veroffentlich, Siemens Werken*, 14, 54-62 (1935).

PERMEABILITY

During the past few years, a great deal of effort has been expended on the study of the permeation of moisture and water through organic protective coatings. Erich Manegold, in a series of papers published over the last ten years in *Kolloid Zeitschrift,* has reported his investigations on the fundamental relationships underlying the phenomenon of permeation of gases and liquids through capillary systems in general. With regard to paints, two general methods of examination are currently in vogue. In Germany, emphasis is placed on measuring the amount of water which a paint film at various ages can imbibe on immersion in water. This is usually referred to as the "swelling number."[33] It has been shown[34] that the "swelling factor" is more significant than the so-called "swelling number." This factor is the ratio of the amount of water taken up by the pigmented film to that absorbed by the unpigmented film. These investigators have also pointed out that this swelling factor is more significant in those paints which do not contain inhibitive pigments. The importance of the proper pigment-vehicle ratio with respect to amount of moisture absorbed has been stressed,[35] as well as the relation between film structure and moisture imbibition. Certain paints may rapidly lose structural strength irreversibly on water sorption, in a fashion resembling certain materials such as blotting papers, whereas other paints may soak up, sponge-like, a considerable quantity of water without serious structural effect. Furthermore, the rate at which water is taken up or lost is important. In atmospheric exposure, these rates may be sufficiently retarded to buffer effectively against transient periods of high humidity. Table 34[13] illustrates the swelling behavior measured in terms of weight-gain of a number of paint coatings which had been exposed 8 years and then immersed for 7 days in water.

Information on swelling numbers must be used with care and judgment. Certain paints may absorb more water than others with the result that significant relations between swelling numbers and durability become apparent. However, moisture sorption and moisture permeation are not necessarily related. It has been pointed out[36] that although some organic materials may absorb only negligible quantities of moisture, they may, on the other hand, permit considerably more moisture to diffuse through them than other materials which absorb appreciable quantities of water.

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[33] Hebberling, H., *Oberflächentechn.*, 14, 1-2 (1937); Droste, W. H., *Angew. Chem.*, 48, 644-7 (1935). Rinse, J., and Wiebols, *Ind. Eng. Chem.*, 29, 1149-54 (1937); Stock, E., *Farben Ztg.*, 42, 1035 (1937).

[34] Wagner, H., and Pabst, E., *Farben Ztg.*, 40, 789, 811 (1935).

[35] Wolff, H., and Zeidler, G., *Farben Ztg.*, 40, 1199 (1935).

[36] Taylor, R. L., Hermann, D. B., and Kemp, A. R., *Ind. Eng. Chem.*, 28, 1255 (1936).

Table 34.—Water-Swelling Behavior of Coatings Exposed 8 Years.[13]

Pigment	Swelling water content in % after 7-day immersion
Zinc oxide	15-30
Zinc oxide—mic. iron 2:3	10-25
Zinc oxide—white lead 7:3	10-25
Aluminum	10-25
Micaceous iron oxide	10-25
Titanium white Std. A.	5-20
Graphite	5-20
Titanium dioxide	5-20
White lead—mic. iron 2:3	3-9
Spanish iron oxide	3-9
I. G. Red B20X	3-9
White lead	1-7
Sulfate white lead	1-7
Red lead	1-7

A method of examining paint coatings for their moisture diffusion characteristics has been extensively employed in this country.[37] In general, the paint film to be tested is mounted on a suitable base material, such as fine-meshed metal screens, Glassine paper, Cellophane, etc., and used as a membrane between atmospheres maintained at different relative humidities and temperatures. Usually, one day is permitted for attainment of a dynamic equilibrium, after which reliable determinations of moisture transfusion are obtained. The moisture contents of the air on the two sides of the membrane are kept sufficiently far apart to establish a steep diffusion gradient. The vessel over which the membrane is sealed may either be desiccated or else contain a material having an appreciable water vapor pressure. The weight loss or weight gain of the diffusion cell is determined. Several investigators have examined the aging characteristics in relation to permeability and find in general that an initial high permeability is followed during the early period of aging by a reduction in permeability and

Table 35.—Permeability of Moisture Through Organic Coatings.

Coating	Milligrams of H_2O/0.001 inch film/sq. inch 24 hours
Cellophane (not moisture-proof)	>300
Cellulose acetate	>300
Vinyl acetate	115
Vinyl chloracetate	27
Linseed oil	80
Long oil varnishes	36-48
Long oil varnish+Aluminum powder	14
Short oil varnishes	17-24
Single-pigment paints	29-56
Nitrocellulose lacquers	15-87
Orange shellac	16
Asphaltic coating	5

[37] Wray, R. I., and Van Vorst, A. R., *Ind. Eng. Chem.*, 28, 1268-9 (1936): Wing, H. J., *ibid.*, 28, 786 (1936); Edwards, J. D., and Wray, R. I., *ibid.*, 28, 549-53 (1936); Payne, H. F., and Gardner, W. H., *ibid.*, 29, 893-8 (1937); Kittelberger, W. W., *ibid.*, 30, 328 (1938); Dantuma, R. S., *Verfkroniek*, 10, 57 (1937); Kline, G. M., *J. Res. Natl. Bur. Standards*, 18, 235-49 (1937); Hague, A., *Natl. Paint Bulletin* 1, 16-17 (July, 1937); 10-11 (Aug., 1937).

then an increase as the film begins to fail by cracking, checking, etc. For this diffusion technique, pore-free films are a requisite and great care is taken to obtain perfect films and perfect edge seals. Table 35 lists typical values illustrating the permeability of a variety of organic films. The coatings were approximately one month old, and were deposited at a thickness of 0.001 inch on Cellophane. The diffusion experiments were conducted at a differential humidity of 90 per cent and at a constant temperature of 25° C.

The moisture permeability of a series of paints, in which various single pigments were incorporated in a common vehicle at a concentration of 25 per cent by volume, is shown in Table 36. The films were approximately one month old. The difference between reactive pigments, such as zinc oxide and red lead in contrast to non-reactive pigments, is clearly indicated.

Table 36.—Moisture Permeability of Various Pigments.

Pigment	Milligrams of H_2O/0.001 in. film/sq. in./24 hours
Clear vehicle	72.3
Silica	40.3
Ochre	38.3
Ferrite L	74.7
1195B Red oxide	55.0
1212 Red oxide	53.6
Black iron oxide	35.7
Chrome oxide	41.6
B.C. white lead	45.5
Basic lead chromate	56.
Lead titanate	47.0
Graphite	40.3
Lampblack	41.7
Zinc chromate	47.7
XX Zinc oxide	34.4
Red lead	28.8

The diffusion studies have shown that the moisture permeation of perfect coatings essentially obeys Fick's diffusion law, in that the amount of moisture permeating is dependent linearly on the thickness of coat. In practice this means that the thicker the organic coating, the better the moisture-excluding ability of a given paint, provided the coating is continuous and free of defects. However, the complete exclusion of moisture cannot be realized even with paint coatings having no defects, and other things being equal the less permeable coatings should show better durability. Unfortunately, however, in paint technology "other things" are seldom if ever equal. There is always the opportunity for a number of other variables to creep in from the moment a given coating is applied until it finally fails to protect. It is the responsibility of the paint technologist to segregate these variables and to develop a better understanding of the several mechanisms by which the protective life of paint coatings is being shortened.

STRUCTURAL PROPERTIES OF ORGANIC COATINGS

The durability and service behavior of all organic coatings is to a large extent determined by the physical structure of the coating and the manner in which this structure changes upon aging. This, in turn, is dependent on the composition of the finishing material, both the continuous phase, the vehicle, and the discontinuous phase, the pigment, playing a determining part. The rate of change in structure is in addition influenced by the environmental variables.

Considerable progress has been made within the past few years in attempting to relate the composition of organic finishes to their structure. Researches in the field of organic polymers of high molecular weight have been particularly helpful in understanding the structure of the continuous phase of the finishing media. Two general classes of polymers are now recognized, namely, the polycondensation resins and the chain polymers.

The polycondensation type of resin forms macromolecules characterized by a three-dimensional network structure. The phenolformaldehyde, urea-formaldehyde and certain of the alkyd resins are typical examples of this class. These resins, when completely condensed, show only moderate tensile strengths and low elasticity. It has been pointed out[38] that their actual tensile strength falls far short of the theoretical tensile strength, which would be obtained if ruptures occurred only at primary valence linkages. To account for this difference, a "Lockerstellen" theory has been postulated, similar in principle to that which Smekal has developed to account for the low actual tensile strength of crystalline solids. These large three-dimensional molecules are also characterized by infusibility and insolubility. When such resins are incorporated in coatings, this is generally reflected by a decrease in permeability to reactive vapors and liquids. Varnishes containing such resins, or coatings made directly from solutions of these resins, find extensive and increasing use for improved resistance to severe exposure conditions.

The chain polymers are characterized by a two-dimensional configuration of their molecules. These polymers consist of string-like molecules having a large ratio between their length and cross-section. In such a resin, the length of the molecular chain and the distribution of chain lengths effectively determines the physical structure properties of coatings made from them. As the molecule grows in average length, the opportunity for development of micellar aggregates or bundles of these string-like molecules is increased. Also, with increasing length of chain, the resin gains in tensile strength and toughness. Most of the resins in this category exhibit high elasticity at certain temperature levels. By high elasticity is meant the type of elasticity exhibited by vulcanized rubber at room temperature. Whereas most solids show an elasticity not much in excess of 1 per cent, these resins, at suitable temperatures, may show an elastic range as high as several hundred per cent. This type of resin, in contrast to the three-dimensional type of polymer, also shows the phenomenon of high viscosity in dilute solutions which, according to Staudinger, is attributable to the large spherical volume of solvent bound during rotation of the molecule on its long axis.

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[38] Houwink, R., *Trans. Faraday Soc.*, 32, Pt. I. 122 (1936).

Coatings made of very long-chain molecules are characterized by tough films, that is, films which exhibit both high tensile strength and high elongation. The nitrocellulose lacquers owe their high film strength primarily to the presence of the long nitrocellulose molecules, derived from the very long cellulose molecule by suitable chemical treatment. There is a clear-cut relation between the viscosity of a nitrocellulose solution and the average chain length of the nitrocellulose molecules. This in turn is reflected in the tensile strength of the films, the low-viscosity material having an appreciably lower strength than the high viscosity material. Owing to the large amount of surface which molecules of this type possess, a good opportunity is offered for adsorptive forces along the surfaces of these molecules to come into play. Thus, in chain polymers, solvents, particularly plasticizers, as well as resins, are firmly held. The addition of a plasticizing component imparts plasticity to the otherwise elastic film by furnishing an improved opportunity of slip between the long-chain molecules or micellar aggregates of them.

The chain polymers remain permanently soluble and fusible. Their solubility in general diminishes as the average length of the molecule increases. However, all these resins, as might be expected, are much more temperature-sensitive in their mechanical characteristics than is the three-dimensional type of structure. Although the physical behavior of the resin is primarily determined by the average length of the molecular chain, the chemical composition of the base unit making up the chain does play a deciding part not only on the specific solvency of the resin, but also on its sensitivity to moisture. Thus, a non-polar resin, such as styrene, is soluble in non-polar solvents and absorbs practically no water. More polar resins, on the other hand, such as the poly-acrylates or the vinyl acetates, are soluble in polar solvents and imbibe considerably more water.

According to the later theories, the drying oil films eventually develop the structure characteristic of the three-dimensional type of polymer. However, there is a slow, gradual transition from a soft and relatively elastic type of film to a hard, brittle and relatively insoluble type of structure. It requires years to effect this transition, and its speed is determined both by compositional and environmental factors. In drying-oil paints, the choice of pigment plays a very important part in modifying the structural characteristics of the coatings. During the early life of a drying oil film, the organic vehicle is quite susceptible to a number of possible reactions. The early oxidation period is accompanied by the splitting off of a number of decomposition products, many of which are reactive. The film at this stage is relatively permeable to moisture and thus provides an opportunity for reaction with either the base metal or the pigment.

The selection of driers also plays an important part at this stage of film formation. Drying oils, which are partially pre-polymerized, such as the bodied stand oils, on application accelerate the formation of a more desirable film structure, both from a physical and chemical standpoint. Drying oils made up of conjugated double bonds, such as tung oil or oiticica oil, form less permeable films than linseed or perilla oil. From a durability standpoint, the problem with various drying oils or modifications of them consists in selecting the optimum compromise between permeability and physical toughness. As J. S. Long pointed out several years ago, the ideal drying oil would quickly oxidize to a point where a tough, hard elastic film is formed; but further change, such as the gradual conversion of the plasticizing liquid phase to the completely brittle end stage, would not occur.

Varnishes

In varnishes, the preformation of large, tough and non-reactive molecules or molecular aggregates is carried to a further stage by the incorporation of suitable resins in a bodied drying oil medium at high temperatures. Here again the problem is to obtain a finishing material which will be less permeable and tougher than a drying oil film, but will not become too brittle in too short a time. Within the past few years it has become the practice to reinforce drying oils with small quantities of a suitable varnish resin. By this means the initial drying time is shortened, permeability to moisture and other reactive gases reduced, while at the same time durability may actually be increased.

Varnishes and varnish-like synthetic resin solutions are frequently subjected to a baking operation immediately after application. This baking operation brings about a number of radical changes in the structure and consequent serviceability of these coatings. First of all, initial adherence is greatly improved owing to the higher mobility of the adhesive constituents in the hot finishing material. The escape of solvents or other weakly held components is facilitated, and thus a closer arrangement of the resin molecules is made possible. High temperature facilitates the curing of condensation resins to their "C" or end state; and in the case of the drying oil components, the tendency to oxidation, with its attendant release of undesirable short-chain molecules, is minimized, whereas the polymerizing opportunity is enhanced. These changes are reflected in the physical character of baked coatings, where hardness and frequently toughness are definitely increased by the baking operation. The formation of molecular aggregates, visible under high-power magnification, has recently been demonstrated.[39] These aggregates were developed upon baking and, when given opportunity for proper alignment, produced films of considerably increased strength. It is also of interest to note that baking permits the development of continuous non-permeable films at a thickness considerably less than is possible with coatings formed at lower temperatures. Furthermore, the minimum thickness at which this continuity was obtained was found to be a function of the materials making up the metal-resin film interface.[40]

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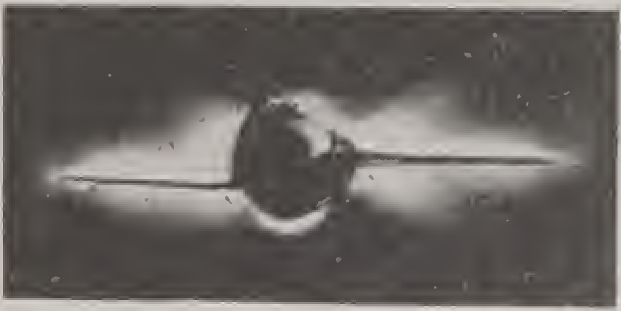
[39] Bender, H. L., *Ind. Eng. Chem.*, 29, 1130 (1937).

[40] Young, G. H., Schneider, W. K., and Gerhardt, G. W., *Ind. Eng. Chem.*, 29, 1280 (1937).

Bituminous Materials

Coating materials of a bituminous nature are characterized in general by low tensile strength and high elongation. This high elongation is mostly of a plastic rather than an elastic nature. The flow behavior of bituminous coating materials is attributable to the composition of this class of material, which consists essentially of a heterogeneous conglomeration of molecules and molecular aggregates, the average size of which is intermediate between that of most resins and pure organic compounds.

The customary method of examining the structural characteristics of organic coatings is to subject them to various mechanical deformation stresses. Suitable devices, similar in principle to those employed in the study of metals, have been developed for the measurement of tensile strength and elongation. A number of other tests have been developed [41] for the application of controlled stresses at various rates, to measure such properties of the coatings as hardness, ductility and impact resistance. These physical tests have served to reveal an enormous difference in resistance to deforming stresses between the various coating materials. As will be shown at a later point, use is made of such tests to provide a quantitative means of evaluating the quality of organic coatings, by measuring the changes in these physical properties with progressive aging of the finishes. With suitable precautions, the effect of any one variable, such as composition, environment, surface preparation, thickness of coating, etc., can be isolated and quantitatively observed.



Courtesy Reinhold Publishing Corp.
From *Chemistry of Synthetic Surface Coatings*, Krumbhaar.

Figure 69.—Tensions Alongside the Cracks in a Film Subjected to Tensile Stress When Observed Under Polarized Light.

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[41] Husse, W., and Zierold, *Farben Ztg.*, 35, 334 (1930). Dantuma, R. S., *ibid*,. 14, (1932). Pfund, A. H., *Proc. Am. Soc. Test. Mat.*, 25, 393 (1925). Nelson, H. A., *Proc. Am. Soc. Test. Mat.*, 21, 1111 (1921). Schuh, A. E., *Ind. Eng. Chem.*, 23, 1346 (1931). Schuh, A. E., and Theuerer, H. C., *ibid, (Anal. Ed.)*, 6, 91 (1934). Blom, A. V., *Angew. Chem.*, 46, 411 (1933); *Chem. App.* 24, 65 (1937); *J. Oil Colour Chem. Assoc.*, 20, 195, 219 (1937); *Paint & Var. Prod. Man.*, 13, 1, 7 (1935). Tasson, F., *Researches et Inventions*, 17, 189 (1936). Van Heucheroth, A. W., *Natl. Paint Varn. Lacq. Assoc. Circ. No. 520*, 282 (1936). New, G. F., *J. Soc. Chem. Ind.*, 56, 261T (1937). Hunt, J. K., and Lansing, W. D., *Ind. Eng. Chem.*, 27, 26 (1935). Rossmann, *Farben Ztg.*, 42, 210 (1937).

In addition to these mechanical attributes of organic coatings, it has been emphasized[42] that the optical properties are of importance. Many films under tension exhibit birefringence, owing to the alignment of the macromolecules under a unidirectional stress. This is shown in Fig. 69. By the use of circularly polarized light, it has been possible to observe local strains as a result of pinholes, extraneous matter, or poorly wetted pigments in the clear films.

Evaluation of Durability

Because of the many factors that influence the durability of organic coatings, and of the fact that good paint coatings require a relatively long time to deteriorate, evaluation of the durability of these coatings has been an active subject among paint technologists for a number of years. Basically, every paint job provides a generous test specimen. However, the opportunity for control of application and for observation of performance of the paint coating is so limited as to make a collection of reliable comparative results by such a method next to impossible. Consequently, two general schemes for evaluating the relative durability of different paint coatings have been developed. One consists essentially of exposure tests, either at carefully selected test sites or by means of accelerated cycles conducted in appropriate test devices. The exposure method of testing relies primarily on the careful recording of visual evidence of degradation. Another method, which has more recently come into use, consists of evaluating the physical changes taking place in the course of exposure and attempting to relate these changes to exposure life. In this method it is not necessary to await the appearance of visual signs of decay of the coatings, inasmuch as the symptoms leading to such evidences can be clearly recognized at an early date.

Exposure Testing

In order to bring under better control a number of the variables that operate in determining the life of a paint coating, it has become customary for paint technologists to make extensive use of test fences in various parts of the world, where test panels, usually prepared under well-defined conditions, are exposed. In order to diminish further the effect of chance variables, exposure tests are usually run in which series of duplicate panels are compared. In general, the more such a testing scheme approaches statistical proportions, the more reliable the observations become. Inasmuch as the climatic factors during exposure exert a powerful influence both on direction and speed of degradation, considerable caution must be exercised in attempting to take the results obtained from one location and apply them to another. In Germany, one group of investigators is using six exposure locations, distributed in various parts of Germany and the difference in durability of the same coatings exposed at these different locations is found to be of a minor order. In this country, however, test fences are scattered over various parts of the country, and, as might be expected, the behavior of similar paints in different locations is quite different. The Iron and Steel Institute of England has test plots scattered over various parts of the British Empire, and consequently a still greater variation in the behavior of the test panels is observed.

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[42] Blom, A. V., *Chem. App.*, 24, 65 (1937).

Besides these far-flung climatic differences, there are local environmental factors which affect durability and hence must be taken into account in exposure tests. For instance, in test fences located in as small an area as England, local exposure differences, such as proximity to the sea or proximity to manufacturing centers, may cause the same paint to fail much more quickly than if it were exposed in a quiet rural section. In fact, according to the British paint technologists, the amount of SO_2 contained in the air may outweigh the importance of differences in average temperature and humidity ranges. Perhaps even more important than the environmental conditions is the surface condition of the metal panels. The presence of rust, scale, or other surface impurities may overshadow in importance both composition of the paint and the effect of environment. In addition, significant variables may enter in the application of the paint. One investigator[43] has enumerated at least twenty variables that affect the evaluation of paint tests and has classified them with respect to preparation and application conditions, panel-exposure conditions, and finally, interpretation of the results.

With paints, particularly, it has been found that the time interval between application of the paint and of exposure, or the time allowed between coats of a paint system, is important. Thus it has been shown[44] that the corrosion of a red oxide paint was reduced about threefold by extending the time interval between painting and immersion in tap water from 11 days to 6 months. In another study it has been shown[45] that the resistance to attack by SO_2 fumes of a freshly applied coating is very poor initially, but soon becomes excellent, developing a maximum resistance at somewhere between 11 and 18 days. In a multiple-coat paint system, it has been consistently found that it is better to permit several days to elapse between coats than to apply the coats in rapid succession.

Exposure tests of protective paints for metals are usually conducted as follows: Metal panels are carefully cleaned to remove surface impurities of both inorganic or organic nature. The size and shape of the panels may vary considerably. In general, flat panel stock is used, although more recently in Germany a new type of test panel is coming into use. This consists of a metal strip 90 centimeters long and 30 centimeters wide. A central 50-centimeter section is maintained in a horizontal position, while one end is exposed to the south at an angle of 45° and the other 20-centimeter end, facing north, is bent at right angles. This type of panel permits six exposure areas to be kept under observation at one time. Usually the edges and backs of test panels are protected, in order to minimize extraneous edge effects. However, some investigators prefer exposed edges and even at times leave an unpainted strip at the top of the panel in order to simulate more closely the practical exposure conditions in which mechanical damage to the paint films is frequently unavoidable. Other practical conditions are at times simulated in test panels, such as the inclusion of sharp bends, rivets, etc. Usually, test panels are exposed with an angular inclination to the south of 45°; depending upon the latitude of exposure, this brings about an acceleration of failure of roughly 2 to 1, compared with vertical exposure.

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[43] Ashman, G. W., *Ind. Eng. Chem.*, 28, 934 (1936).

[44] Friend, J. N., and Griffin, B. L., *J. Color Chem. Assoc.*, 9, 1106 (1926).

[45] Peters, F. J., *Farben Ztg.*, 39, 675 (1934).

After the panels are cleaned, the series of paints to be compared is carefully brushed out to as even a film as possible. Variations in film thickness unquestionably influence the rate of failure. As previously shown, resistance to water permeation and the development of local stresses is influenced by thickness of coating, and with thin-brushed coatings an appreciable variation in coating thickness from point to point may readily result. In fact, in a recent report of a long exposure test [13] it was pointed out that the chief source of discrepancy between duplicate panels was attributable to these variations in film thickness. If a large series of test panels is to be exposed, care must be exercised in rotating the schedule of application so that the length of time between application of the priming coat, the top coats, and the beginning of exposure will be approximately the same for all the panels. Most laboratories have adopted conventional forms for recording the visual observations at suitable time intervals. On such forms, evidences of chalking, color change, checking, cracking, flaking and rusting are recorded. At times, photographic records, sometimes enlarged, are taken to assist in the preservation of observations.

It depends very much on the nature of the service expected of the coatings under test as to which type of appearance change deserves most emphasis. Thus, test panels of automobile finishes will place a premium on color and gloss changes. On the other hand, with a rust protective paint for large immobile structures, such surface changes would be relatively unimportant, and rusting would be very important. The relative emphasis to be placed on various visual changes must arbitrarily lie in the hands of each investigator and it is a matter of some difficulty to reach agreement as to proper interpretation of the results.

Results of Exposure Tests

Within the past 25 years, many exposure series, involving thousands of test panels, have been carried through by various technical organizations. The results of some of these have been published and of these, three series will be discussed.

In the years 1908 to 1915 the American Society for Testing Materials exposed several hundreds of steel panels at Atlantic City. Single-pigment paints were prepared at an approximately equal pigment volume in a vehicle consisting of $\frac{2}{3}$ raw and $\frac{1}{3}$ boiled linseed oil. The test fence was examined periodically by a coöperative group of paint technologists and the degree of rusting recorded. The results are shown in Table 37, which summarizes the report[12] of the Committee, number 10 in the table indicating the highest rating and 0 the lowest. Many of these paints would normally be restricted to use as primers, and hence their relative rating as protective paints when used also as top coats is at variance with general evaluation. As can be seen from this table, many of the pigments which showed an inhibitive tendency in water immersion tests also showed good durability on exposure, and in addition, a number of the rust stimulating pigments failed early on exposure. However, several of the pigments behaved quite inconsistently with their behavior in the water tests. In this particular exposure series, American vermilion, a basic lead chromate pigment, gave

Table 37.—Exposure vs. Laboratory Corrosion Tests.[12]

Pigment	Classification in Water Tests	Average rating of oil (exposure) tests				
		1910	1911	1912	1913	1914
Dutch process white lead	Inhib.	8.7	3.7	1.9	1.3	a
Quick process white lead	Indet.	8.9	4.2	2.1	1.3	a
Zinc oxide	Inhib.	3.0	1.5	0.7	0.8	a
Sublimed white lead	Indet.	9.5	9.0	8.1	5.9	3.5
Sublimed blue lead	Indet.	9.6	8.8	9.0	7.2	6.0
Lithopone	Indet.	4.1	2.2	0.8	0.4	a
Zinc lead	Inhib.	8.0	4.7	4.5	3.3	a
Orange mineral	Indet.	9.0	8.3	6.9	4.0	3.0
Red lead	Indet.	8.7	8.3	8.1	6.3	4.0
Bright red oxide	Stim.	9.3	8.1	6.7	4.5	2.5
Venetian red	Indet.	7.2	8.0	6.4	5.1	1.5
Metallic brown	Indet.	6.3	6.3	6.2	6.1	3.0
Natural graphite	Stim.	9.1	6.8	6.6	6.2	4.0
Artificial graphite	Stim.	7.1	5.9	4.4	2.6	0.0
Lampblack	Stim.	7.1	6.3	5.5	4.2	0.0
Willow charcoal	Inhib.	8.8	8.8	8.6	7.9	4.5
Carbon black	Stim.	8.3	7.2	7.0	6.8	5.0
Yellow ochre	Stim.	5.8	5.5	5.8	5.2	1.5
Barytes (natural)	Stim.	4.4	0.7	0.3	0.1	a
Barytes (precipitated)	Stim.	4.1	1.8	0.7	0.2	a
Calcium carbonate (whiting)	Indet.	0.1	0.0	0.0	0.0	a
Calcium carbonate (precip.)	Indet.	0.0	0.0	0.0	0.0	a
Calcium sulfate (gypsum)	Indet.	2.5	1.7	0.9	0.2	a
China clay	Indet.	7.3	6.3	2.7	1.3	a
Asbestine	Indet.	7.3	5.1	1.9	1.2	a
American vermilion	Indet.	9.1	10.0	9.9	9.8	7.5
Medium chrome yellow	Indet.	7.0	7.7	6.0	5.2	3.5
Zinc chromate	Inhib.	9.4	9.5	8.8	8.0	4.0
Zinc and barium chromate	Inhib.	9.7	9.5	8.5	7.8	2.5
Chrome green	Inhib.	9.8	9.8	8.6	7.6	5.0
Prussian blue (water-stimulative)	Stim.	9.2	9.0	7.8	6.7	3.5
Prussian blue (water-inhibitive)	Inhib.	8.8	8.5	7.2	5.0	a
Ultramarine blue	Inhib.	4.0	0.0	0.0	0.0	a
Magnetic black oxide	Unclass.*	9.5	9.5	8.6	7.8	4.0
Zinc and lead chromate	Inhib.	9.5	9.7	9.2	8.3	4.0

a Panels removed from fence in 1913.

* This pigment was not included in the original water tests, and its classification is not given or taken into consideration in the averages. It was included in the field tests at the suggestion of S. S. Voorhees. It proved in later individual tests to be water inhibitive.

the best performance record of all the pigments examined. Whereas a number of subsequent exposure tests conducted by other technical groups have rated basic lead chromate as a good priming pigment, in no other case was its superiority so clearly demonstrated as in this Atlantic City test. Furthermore, paints containing natural graphite, willow charcoal and carbon black showed good durability in this test, whereas in other studies such paints have given satisfaction only over good inhibitive priming coats.

More recently, the results of an 8-year exposure test program conducted in Germany have been reported.[13] The pigments examined were red lead, iron oxide, basic carbonate, white lead, sulfate white lead, leaded zinc oxide, titanium dioxide (2 kinds), micaceous iron, aluminum powder and graphite. The vehicles examined were linseed oil, linseed oil stand-oil, and a mixture of linseed and tung oil stand-oil (20 per cent tung oil). These paints were applied in 3 coats in various combinations of priming coat and top coats, and several pigment combinations in either the priming coat or top coat were included. The unexpected result of this study is that, with the exception of the pure titanium paints, practically all the panels after 8 years of exposure are still in excellent condition from a rust protection standpoint. This, in the opinion of the authors, is largely attributable to the care exercised in the preparation of the test panels before exposure.

Although these tests are being continued, several rather important conclusions have become evident. Stand oils, and particularly the bodied linseed-tung oil combinations in top coats, have given better corrosion protection than the corresponding linseed oil paints and thus permit the safe use of a larger number of pigments in protective paints. The relative protective quality of the pigments in this series is summarized in Table 38.

Table 38.—Rust Protective Action of Pigments in Linseed Stand-Oil After 8 Years' Exposure.

Two Coats on Iron	Two Coats on Red Lead Primer	Rust Grade*
Carbonate white lead	Carbonate white lead	0
Sulfate white lead	Sulfate white lead	0
Zinc oxide (LX 81.3 ZnO, 19% $PbSO_4$)	White lead—micaceous iron oxide	0
Zinc oxide S—White lead 7:3	Zinc oxide L	0
Zinc oxide S—Mic. iron oxide 2:3	Zinc oxide S	0
	Zinc oxide S—white lead 7:3	0
	Zinc oxide+micaceous iron oxide 2:3	0
Aluminum	Aluminum	0
Zinc oxide S	Spanish iron oxide	0
Spanish iron oxide	Micaceous iron oxide	0
White lead—mic. iron oxide 2:3	I.G. red B20X (synthetic FeO)	1
I.G. red B20X	Titanium white (Std. A)	1
Titanium white (Std. A)	Graphite	2
Titanium dioxide (pure)		2
Graphite		3
Micaceous iron	Titanium dioxide (pure)	4
Aluminum (1 coat)		5

* Method of grading: Grade 0 = perfect; grade 5 = general failure.

In many cases the propagation of rust beneath the paint was slower in paints containing lead pigments than in those without lead pigments. Although the high quality of red lead as a priming pigment was confirmed, it is possible to use a lead-free paint system of satisfactory durability. Such a system might consist of an iron oxide paint as a priming coat, followed by two top coats containing zinc oxide or a zinc oxide-micaceous iron oxide mixture, the vehicle in the system consisting of a stand-oil rather than ordinary linseed oil The relation between thickness of coating and quality of protection is of interest and it was found that most of the discrepancies in the performance of duplicate test panels was attributable to variations in thickness.

The Corrosion Committee of the British Iron and Steel Institute is conducting a comprehensive test program on protective paints for metals. In this investigation twelve exposure stations were chosen in various parts of the Empire in order to provide a diversity of environmental conditions. At the end of six years, the following conclusions were drawn:[46]

The proper surface preparation of iron and steel prior to painting is most important. Complete scale removal, either by pickling or sandblasting, is definitely preferred over partial weathering followed by hand-cleaning; it may increase the life of a paint system 50 per cent or more. Where feasible, this complete de-scaling should be conducted at point of fabrication, where also the first coat of paint should be immediately applied. The use of a red lead paint as the priming coat has given the best results and is preferred to a non-inhibitive primer.

Paints applied to copper-bearing steels have lasted longer than on ordinary steels, inasmuch as failure has been found to be retarded when once begun. However, this advantage is doubtful if proper surface preparation and effective maintenance is practiced. Although the use of paints for protecting iron and steel structures has given satisfactory and economical results in most locations, under certain conditions, such as exposure in the tropics, the use of protective metallic coatings offer good possibilities.

Accelerated Exposure Tests

The chief limitations of normal outdoor exposure tests are the length of time required to obtain results and the variation in climatic factors between the various exposure locations. It has been the aim of paint technologists for some years to utilize accelerated exposure tests in which the various outdoor exposure factors could be simulated and intensified. Test devices have been developed in which series of panels can be exposed to a number of different conditions and a large number of such exposure cycles have been tried. Figure 70 illustrates one such device in which test panels are irradiated by an arc light and periodically wetted by a water spray as the drum slowly rotates. In these accelerated tests, panels have been subjected to varying conditions of temperature (from 150° F. to below freezing), humidity (water immersion, water spray, saturated humidity, desiccated atmospheres), simulated sunlight (mercury arc, carbon arc, lamps with various filters) and various corrosive gases (SO_2, ozone, etc.). The cycles have been juggled so that innumerable combinations have been tested.

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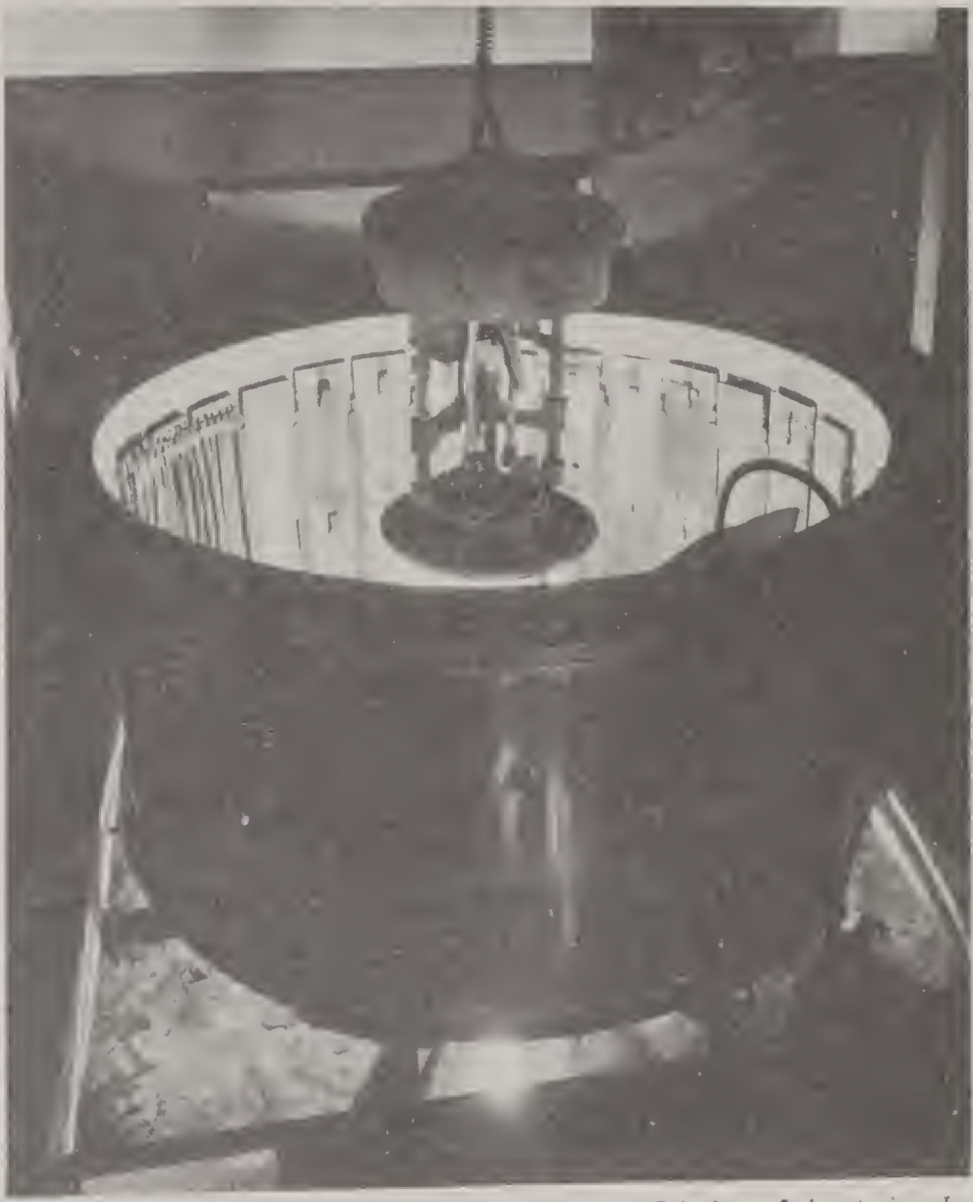
[46] Fifth Report of the Corrosion Committee of the Iron and Steel Institute, London, 1938.

In this country, the American Society for Testing Materials has been particularly active in trying to standardize an acceptable single accelerated cycle suitable for all paint coatings. It is frequently stated that the purpose of accelerated tests is to provide a more speedy degradation of the coatings than is possible by a "normal" exposure. The difficulty with such an aim is that the concept "normal" is a chimerical one, inasmuch as there is no such thing as a norm for paint coatings, either by way of exposure environment or service conditions prevailing in practice. About 15 years ago,



Courtesy of Bell Telephone Laboratories, Inc.

Figure 70.—Accelerated Exposure Test.

the American Society for Testing Materials considered the feasibility of developing a single universal accelerated test cycle, but later came to the conclusion that it was necessary to establish several different cycles, which might be more specifically suited to testing the various classes of organic coatings. After consideration of separate accelerated cycles for metal protective paints, for paints over wood, for nitrocellulose lacquers, and for indoor finishes, it was found that even these individual cycles should be subdivided further to permit the comparison of finishing materials in each class varying widely in composition. A recent symposium[47] on this subject has served to emphasize the conflicting nature of many of the test results that can be obtained by accelerated tests. They have unquestionable value as a means of saving time in a strictly comparative series of tests. However, the experimenter employing such methods must exercise care in the interpretation of results and refrain from offering, at times, untenable generalizations. In accelerated tests there always lurks the danger that speed may be purchased at the expense of validity since a proper balance of accelerating factors is exceedingly difficult to obtain.

Evaluation by Physical Tests

Exposure testing relies almost entirely upon a close following of visual changes. This is true whether the test panels are exposed outdoors or in some artificially accelerated type of cycle. In most organic finishes, these visual changes make their appearance relatively late in their exposure life. With the exception of such superficial appearance phenomena as changes in gloss or color, the more serious evidences of paint film degradation, such as checking, cracking, scaling, flaking and rusting, are preceded by invisible physical alterations within these coatings. These physical changes can be readily detected and quantitatively measured by suitable tests. A method of evaluation, in which such tests are periodically applied in the course of aging of test specimens, relies not so much on an intensification of factors causing degradation in order to gain speed, as it does upon the use of more sensitive tools by which the progress of aging can be followed during the complete history of a coating. Measurement of such physical attributes of coatings as their toughness, that is, their strength, distensibility, and resistance to impact, and their adhesion to the substrate, and particularly a knowledge of the rate of change of these properties, permits forecasting their ultimate life long before failure occurs. Furthermore, much-needed quantitative information on the relation between the several factors affecting the aging processes is obtained. Thus the effect of climatic conditions, which play such an important part in controlling both the direction and speed of the degradation of coatings exposed outdoors, can be accurately estimated. On indoor exposure, where aging effects are more dependent on the inherent composition of the finishing materials, this physical method of evaluation can quickly distinguish between the relative quality of different coating media.

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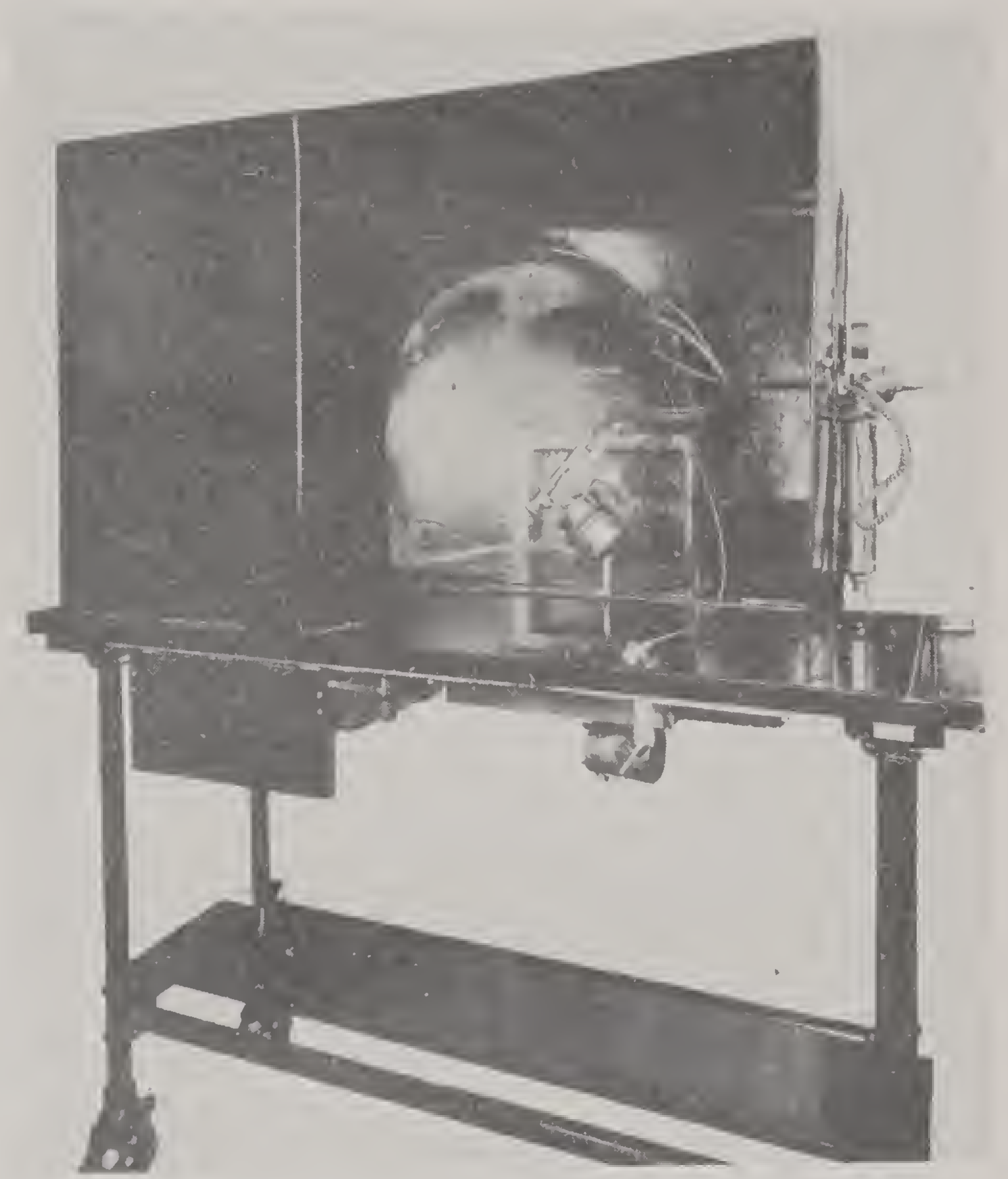
[47] Symposium on Correlation Between Accelerated Laboratory Tests and Service Tests on Protective and Decorative Coatings, *Am. Soc. Test. Mat.*, Philadelphia, Pa., 1937.

The value of applying a physical approach to the evaluation of durability of paint coatings has been recognized by a number of investigators. In this country, Nelson [48] and his co-workers at the New Jersey Zinc Company were the first to use this method of approach. The first important work in this country consisted of subjecting unattached paint films to stress-strain analyses by tensile strength and elongation determinations. By this means a number of interesting and significant relations were shown to exist between composition, tensile strength and elongation as affected by



Courtesy of Bell Telephone Laboratories, Inc.

Figure 71.—Automatic Spray Machine for Producing Films of Controlled and Uniform Thickness.

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[48] Nelson, H. A., *Proc. Am. Soc. Test. Mat.*, 21, 1111 (1921); Nelson, H. A., and Rundle, G. W., *ibid.*, 23, Pt. II, 356 (1923); Nelson, H. A., *ibid.*, 23, Pt. I, 290 (1923); Rundle, G. W., and Norris, W. C., *ibid.*, 26, Pt. II, 546 (1926).

humidity, temperature and aging. Not only the ultimate tensile strength values, but also the shape of the stress-strain curves up to the point of rupture, proved to be important. For instance, in the case of oil paints, the effect of different pigments on the shape of the stress-strain curves and on the ultimate tensile strength and elongation was clearly revealed. In the case of nitrocellulose lacquers, the effect of varying the kind and amount of plasticizer, resin, and viscosity of nitrocellulose was demonstrated. In varnishes, variations in the kind and quantity of resin were clearly reflected.

Owing to difficulties of manipulation, many types of coatings are not suitable for this free-film technique. Furthermore, the method by its nature has the inherent drawback of omitting the important factor that adhesion plays in determining the durability of coatings. This has been largely overcome by the use of tests in which strength and distensibility, as well as the adhesional properties of attached coatings, are measured. The details of several such test methods will be described at a later point.

In order to make the determination of aging by means of periodic physical examination feasible, two general conditions must be observed. The test panels of a series being aged must be equilibrated to the same temperature and humidity conditions at each period that the physical tests are performed. Also, the thickness of the coatings in duplicate panels of a series must be held constant. Fig. 71 [48a] illustrates an automatic spray machine by means of which uniform film thickness can be obtained. All organic coatings are highly sensitive in their physical properties to changes in temperature and relative humidity. By way of illustration, the effect of moderate changes in external conditions on the distensibility of several coatings is shown [49] in Table 39. Variation in thickness has a pronounced effect on the behavior of most organic coatings. Internal stresses produced by the development of structural gradients or by uniform shrinkage effects

Table 39.—Effect of Temperature and Humidity on Distensibility of Finishes.

Coating	Per Cent Elongation at Indicated Relative Humidity at 77° F.			Per Cent Elongation with Indicated Temperature at 50 per cent Relative Humidity		
	26 per cent	50 per cent	90 per cent	55° F.	77° F.	95° F.
10-gal. ester-gum varnish	1.5	4.2	49.9	0.6	4.2	54.0
					2.1*	12.0*
Synthetic air-drying enamel	15.0	15.1	54.9	2.3	15.1	53.2
					2.2*	3.8*
Highly plasticized lacquer	22.5	24.5	31.2	12.9	24.5	31.6
					10.8*	25.7*
Baked synthetic enamel	43.0	42.3	46.6	12.5	42.3	48.9
					6.0*	9.9*

* Coating aged 16 months indoors. In all other cases coating aged 2 weeks. All are approximately 0.001 inch thick.

[48a] Arlt, H. G., *Bell Laboratories Record*, 14, 216 (1936).

[49] Schuh, A. E., *Proc. Am. Soc. Test. Mat.*, 36, 770 (1936).

vary greatly with thickness, and these in turn influence the exposure life, frequently altering the type of failure of the same coating material. In other cases, thickness variation modifies exposure behavior by affecting the ease with which moisture can permeate and the extent to which the coating medium can react with the basis metal. In Table 40 are shown[50] typical values illustrating the effect of thickness on several physical properties after one year of outdoor exposure of various organic finishes.

Table 40.—Effect of Thickness on Physical Properties of Various Coatings.*

Coating	Thickness (in 0.001 inch)	Abrasion Value (Grams of abrasive per 0.001 inch)	Impact Res. (r.p.m. of impact hammer)	Hardness (Load in grams for fixed indentation)	Extensibility (% Elongation at 1st rupture)
25-gal. ester-gum varnish	0.6	17	900	640	25.5
	3.5	41	255	7	>60
Air-drying synthetic resin varnish enamel	0.5	1	<185	>800	1.8
	3.6	15	<185	175	2.0
Air-drying synthetic resin varnish enamel	0.5	24	<185	710	30.0
	3.5	59	400	220	14.8
Nitrocellulose lacquer enamel	0.6	21	>1500	760	3.0
	3.1	24	1500	480	18.2
Nitrocellulose lacquer enamel	0.5	31	>1500	820	2.9
	3.6	52	900	620	1.7
Baked synthetic enamel	0.5	28	>1500	765	5.6
	2.2	56	>1500	570	3.1
Baked Japan	0.5	41	>1500	840	4.6
	2.9	61	>1500	460	8.8

* These coatings were aged 1 year outdoors.

With these two variables controlled, it is then possible to correlate aging with changes in physical properties, and definite curves depicting such changes with time can be obtained. Periodically, sets of carefully-prepared duplicate panels are subjected to physical tests at the reference temperature and humidity. In the period between tests the panels may be exposed to any desired environment, drastic or mild, depending on urgency for comparative results or the type of finishing materials under examination. By this means, also, an opportunity is provided for comparing quantitatively the effects of different environments on the rate and manner of degradation of various organic finishes.

A number of different tests have recently been developed by which significant physical characteristics of anchored coatings are measured. One of the most important properties of an organic finish is its distensibility. The reason for this may not be at once apparent, inasmuch as the amount of contraction or expansion which a basis metal undergoes with outdoor temperature fluctuations is small indeed, amounting at most to a fraction of one per cent. True enough, over wood, the base material, owing to water sorption, demands a considerably higher minimum distensibility in

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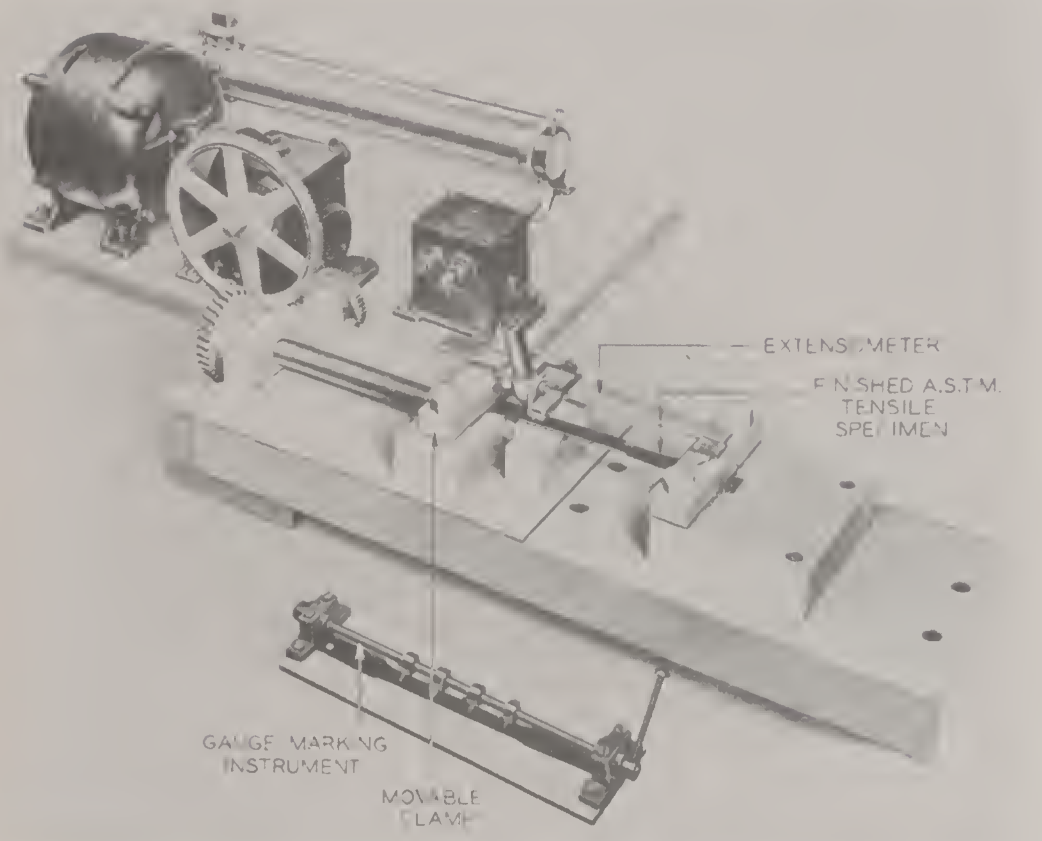
[50] Schuh, A. E., and Theuerer, H. C., *Ind. Eng. Chem.*, 29, 182 (1937).



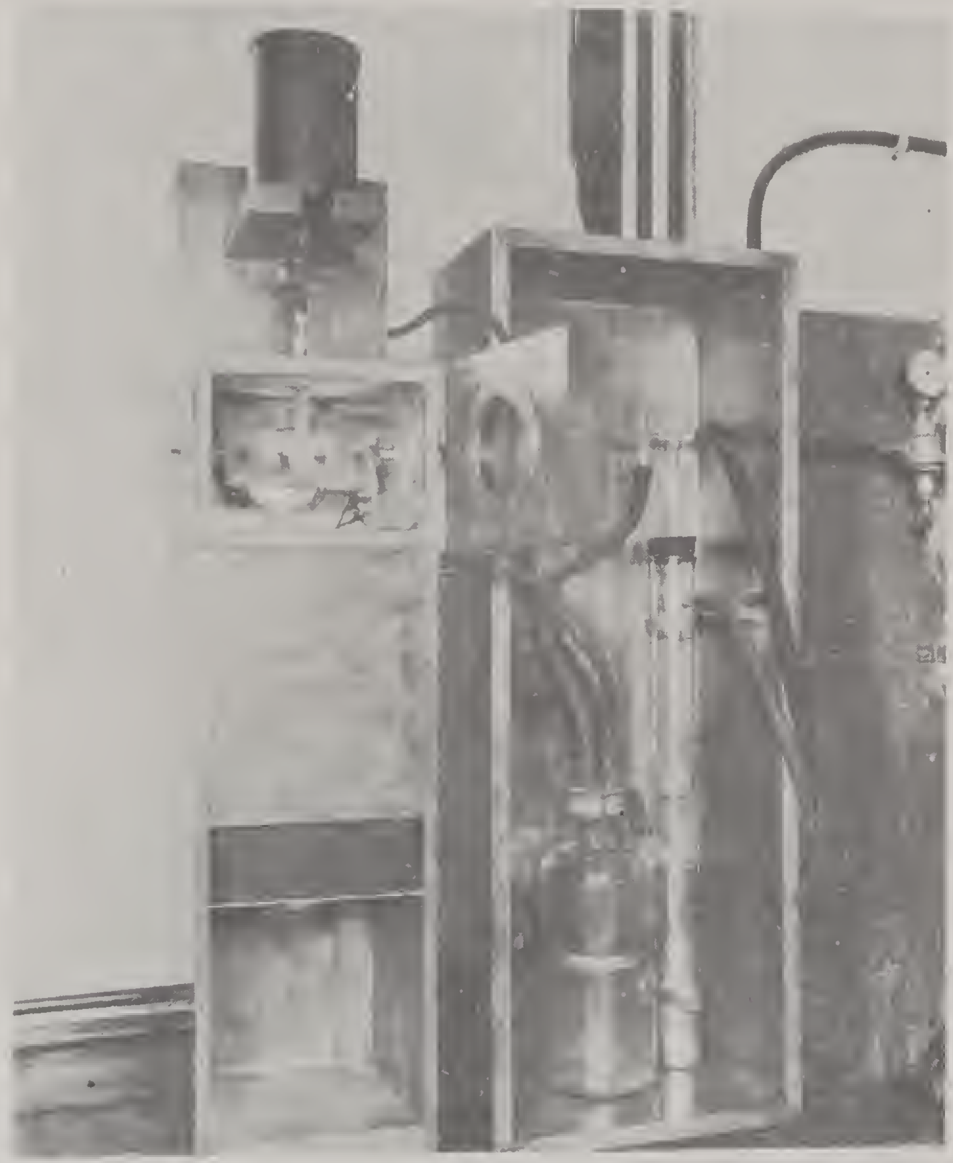
Courtesy of Bell Telephone Laboratories, Inc.

Figure 72.—Device for Determining Distensibility of Attached Organic Coatings.

Courtesy of Bell Telephone Laboratories, Inc.

Figure 73.—Conical Mandrel Test for Determining Distensibility of Attached Organic Coatings.

the coating. The importance of distensibility measurements lies in the fact that they furnish a sensitive criterion for aging. In general, those organic coatings which reach a low distensibility most rapidly also fail the earliest on exposure. Thus certain coatings, such as short-oil varnishes and some resin solutions, one month after application, may show a distensibility of only two or three per cent elongation and fail on exterior exposure after only a few months. Many other materials retain a distensibility of twenty per cent or more for well over a year and give a corresponding exposure life of several years. The distensibility of attached coatings is determined either by direct extension of a suitable test specimen and observation of the per cent elongation at which rupture in the form of microscopic cracks occurs[51] or else by bending over mandrels of known radius



Courtesy of Bell Telephone Laboratories, Inc.

Figure 74.—Abrasion Test for Organic Coatings.

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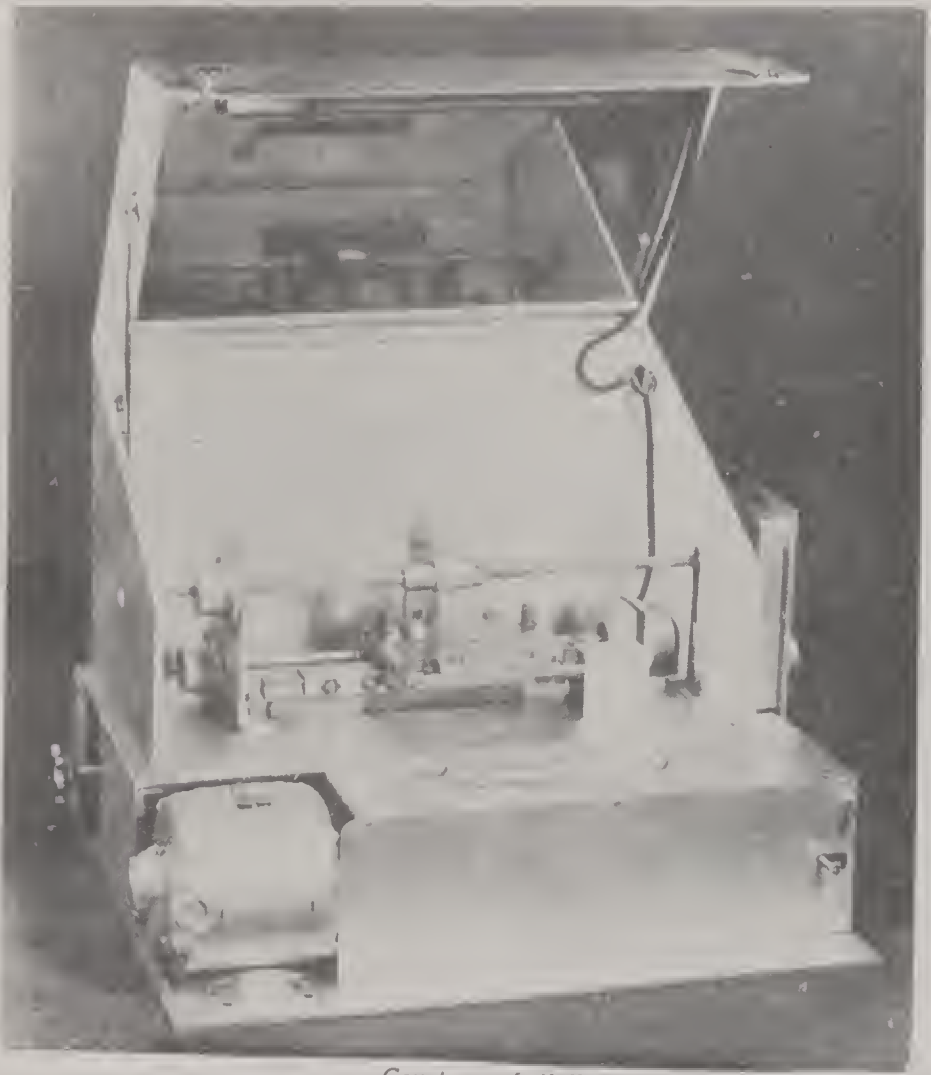
[51] Schuh, A. E., and Theuerer, H. C., *Ind. Eng. Chem. (Anal. Ed.)*, 29, 9 (1937).

and calculating the per cent elongation at first rupture.[52] Figures 72 and 73 illustrate such instruments.

Information on the strength of organic coatings, when examined as attached coatings, is obtained by measurement of their resistance to abrasion under suitable test conditions.[53] In one such test, shown in Figure 74 a coated specimen is subjected to the cutting action of millions of small abrasive particles impelled at controlled velocity against the paint surface. The air which impels these particles serves also to maintain a constant temperature at the zone of abrasion. The abrasion value is a summation of the work done by these particles in pulling the film apart and in that manner serves as an approximate measure of the area under a stress-strain curve, such as obtained by the free-film method. A means is thereby provided of arriving at the effective tensile strength of an anchored coating.



Courtesy of Bell Telephone Laboratories, Inc.

Figure 75.—Impact Machine for Testing Coatings.

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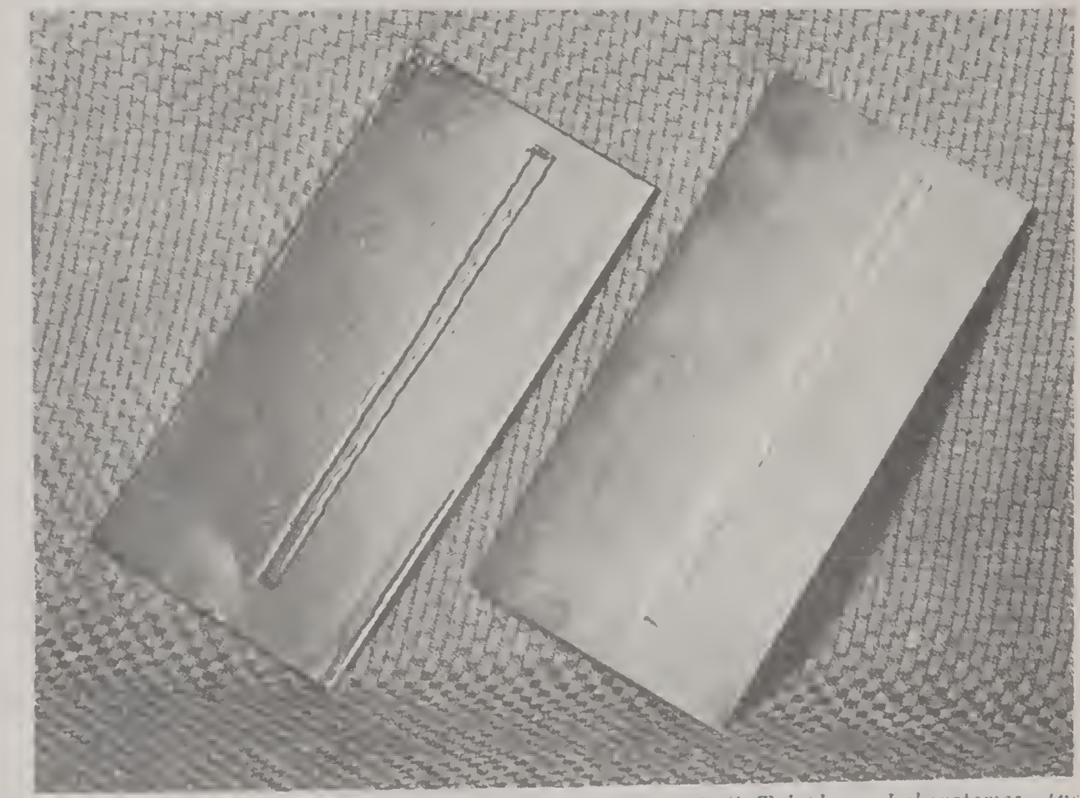
[52] Arlt, H. G., *A.S.T.M. Bulletin*, (Dec., 1937).

[53] Schuh, A. E., and Kern, E. W., *Ind. Eng. Chem. (Anal. Ed)*, 3, 72 (1931).

Both free and anchored film technique have shown that aging of most materials is accompanied by a rise in ultimate tensile strength and progressive loss in elongation.

Impact tests, though necessarily of a somewhat arbitrary nature, serve a twofold purpose. They offer information on the relative resistance of various coatings to deformation in the form of sudden concentrated stresses, and also throw considerable light on the degree to which a coating adheres to its substrate. The effect of various surface preparations on initial adherence is clearly reflected, and changes in adherence, brought about by interfacial reactions at the metal substrate are immediately revealed. In one such test,[54] illustrated in Figure 75, a loosely pivoted, round-headed hammer strikes glancing blows on the panel surface at increasing velocity, and the speed at which it hammers through to the base is noted. (Figure 76.) Brittle materials shatter over considerable areas beyond the point of impact. It may not be generally appreciated that materials, particularly baked synthetic enamels, which exhibit remarkable toughness are now available. Thus in Figure 77 is shown a nail having a specially coated head being driven into a hardwood block without seriously marring the coating on the head of the nail.



Courtesy of Bell Telephone Laboratories, Inc.

Figure 76.—The Type of End Point Obtainable on the Impact Machine (Figure 75). Failure Shown on Panel at Right.

A number of other physical test devices have been developed and are being used in various laboratories.[55] In Table 41 are shown data which illustrate the type of information obtainable by a physical method of evaluating organic finishes. Wide variations in physical characteristics as a function of composition of the coatings are found. In most instances, the protected indoor exposure has brought about a much slower rate of degradation than a corresponding outdoor exposure. At the time when these physical measurements were made, only two of the materials, namely A and D, showed any visual evidence of degradation, such as checking and cracking. It is of interest, therefore, to show the correlation of these data with subsequent visual behavior after exposure for four years. As might be expected from the physical data, the two poorest materials (A and D) failed earliest, and both failed in the same manner, namely by flaking, in six to nineteen months, depending on thickness of coating. The heavy coatings of these two materials failed the soonest. Materials B, C, H, I, K, and M are still in excellent condition after four years of exposure. The remaining coatings failed by flaking after two to three years' exposure,

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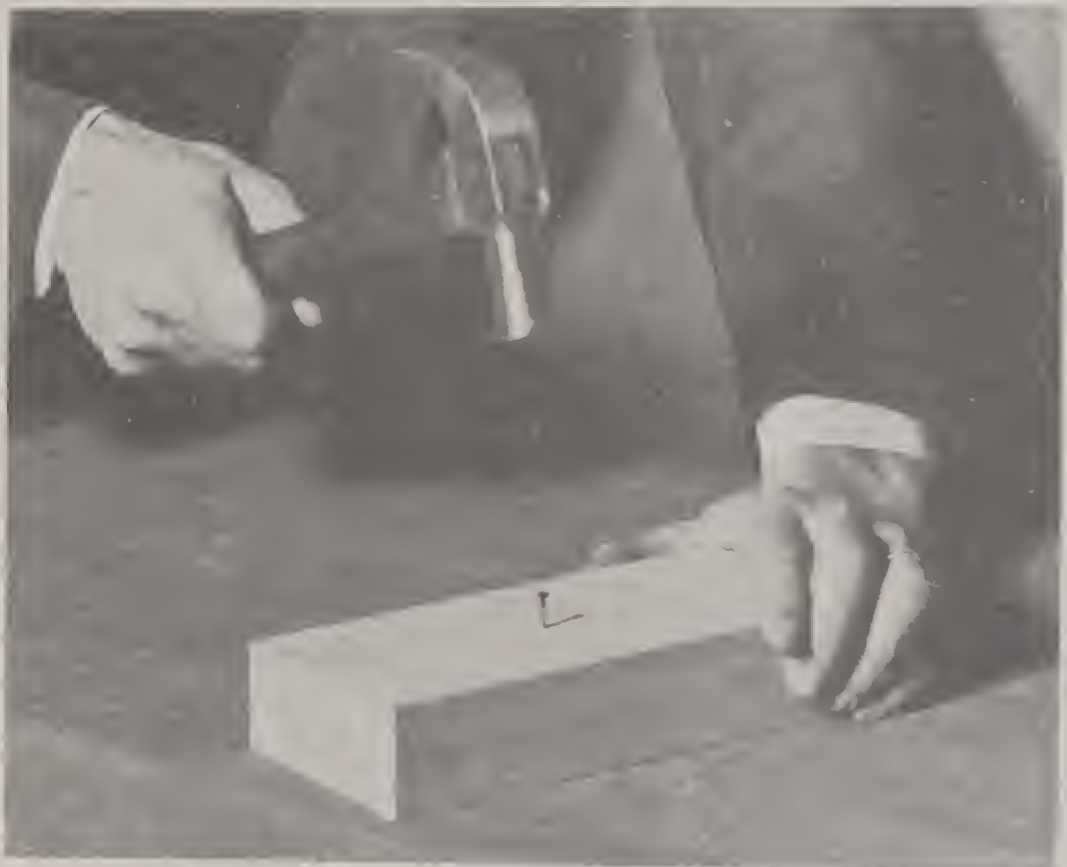
[54] Arlt, H. G., *Bell Laboratories Record*, 15, 108 (1936).



Courtesy of Bell Telephone Laboratories, Inc.

Figure 77.—An Illustration of Impact Resistance.
The nail with specially coated head can be driven into a hardwood block without damaging the coating.

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[55] A brief description of a number of such tests is found in H. A. Gardner's book "Physical and Chemical Investigation of Paints, etc.," 8th ed., Institute of Paint and Varnish Research, Washington, D. C., 1937.

Table 41.—Physical Characteristics of Various Organic Finishes.

Coating	Abrasion Value[1]			Impact Resistance[2]			Hardness[3]			Distensibility[4]		
	I[5]	II	III	I	II	III	I	II	III	I	II	III
Ester gum varnish enamels												
A 10-gal. varnish	8	5	7	270	<185	385	380	>500	500	8.2	2.1	2.1
B 25-gal. varnish	38	34	36	>1500	490	>1500	130	...	285	59.0	48.3	54.4
C 40-gal. varnish	56	42	58	>1500	965	>1500	35	295	47	>60	54.3	>60
Air-dried synthetic resin varnishes												
D	17	2	16	<185	<185	<185	280	...	450	10.2	2.2	1.4
E	55	45	57	>1500	<185	1500	386	490	445	59.1	38.8	46.1
F	42	42	44	300	<185	555	68	500	270	>60	50.3	56.3
G Resin-reinforced linseed oil paint	53	53	57	<185	<185	485	30	94	38	59	41.3	46.3
Nitrocellulose lacquer enamels												
H	24	21	25	>1500	>1500	>1500	720	680	680	29.9	10.8	11.8
I	53	49	56	>1500	>1500	>1500	685	760	660	19.6	6.0	9.8
J	35	30	36	>1500	305	>1500	270	570	320	30.9	5.6	21.1
Baked enamels												
K Synthetic resin	45	27	49	>1500	>1500	>1500	730	690	640	28.2	4.0	24.6
L Synthetic resin	58	43	66	>1500	<185	>1500	135	800	330	>60	5.4	>60
M Japan	60	49	63	>1500	>1500	>1500	530	780	740	24.2	8.8	21.3

[1] Expressed in grams of abrasive required to wear through 0.001 inch of coating.

[2] R.P.M. of impacting hammer required to reveal base.

[3] Pfund Hardness: load in grams required to obtain fixed impression.

[4] Per cent elongation at which coating showed rupture when magnified 10 times.

[5] Columns I, II, and III signify different aging periods: I, coatings one month old, aged indoors; II, an additional period of 13 months outdoors (roof of Bell Telephone Laboratories building); and III, 16 months indoors at 25° C. and 50 per cent relative humidity.

owing to loss in adhesion, which in each case was clearly foreshadowed by the drop in impact value many months in advance of actual visual evidence.

Many of the organic coating materials listed in Table 41 represent the hard type of enamels designed for the protection and decoration of equipment used indoors. The method of physical evaluation is not, however, limited to this class of materials. It has been shown [56] that there is a good relationship between outdoor durability of paints and their retention of distensibility. The need of using priming coats and top coats of comparable physical characteristics to obtain best durability was emphasized. In Table 42 are listed the abrasion and corresponding hardness values of a number of single pigment paints in which the pigments were dispersed 25 per cent by volume in a varnish-reinforced linseed oil vehicle. It can be seen that both red lead and zinc oxide, the two most reactive pigments in this series, exert the strongest effect on abrasion value and hardness. The coatings were only about one month old at the time of test, and the fact that the differences between these paints and the clear vehicle are so large suggests that this method of evaluation, correlated with exposure tests, will provide a fruitful field of future investigation.

Table 42.—Physical Properties of Single-Pigment Paints.[1]

Paint	Abrasion Value [2]	Hardness [3]
Clear vehicle	140	<5
Silica	139	<5
Lead titanate	101	<5
Chrome oxide	88.3	<5
Iron oxide	82.0	10
Iron oxide	69.4	5
Iron oxide	64.5	20
Black iron oxide	82.0	5
Ochre	61.0	5
B.C. white lead	61.1	8
Basic lead chromate	56	12
Graphite	46	5
Lampblack	63.5	40
Zinc chromate	60.0	30
Zinc oxide, XX	69.2	150
Red lead	41.3	97

[1] The pigments were incorporated 25 per cent by volume in a common vehicle, applied to clean steel and about one month old.

[2] Grams of silicon carbide required to abrade through 0.001 inch of coating.

[3] Pfund Hardness: load in grams for fixed impression.

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[56] Jacobsen, A. E., *Offic. Dig. Fed. Paint & Varn. Prod. Clubs* 146, 215 (1935); Robertson, D. W., and Jacobsen, A. E., *Ind. Eng. Chem.*, 28, 403 (1936).

Chapter 15

Paint Practices

In the two preceding chapters the composition and durability of organic coatings for purposes of metal protection have been discussed. At this point some of the more practical phases of the subject will be considered, such as the painting of large outdoor steel structures, the industrial finishing of equipment and apparatus, and the protection of underground pipe structures.

PAINTING OF OUTDOOR STEEL

The investment in steel structures, such as bridges, trestles, large tanks, etc., is usually of such magnitude that economy dictates a method of protection which is effective against rusting for long periods of time. The most common method of preserving these structures is by means of paint. If the cost of painting is broken down into such factors as cleaning, erection of scaffolds, labor, and paint materials, it will be found that the cost of the paint material itself is of relatively minor importance, probably ranging somewhere between 10 and 25 per cent of the total cost of application. This obviously makes it desirable to use the best paint materials, inasmuch as economies effected by the use of cheaper finishing materials can effect only a small relative saving. If the life of an outdoor finish can be extended from four years to five years by the use of a paint of higher quality, this result would justify an increase in the cost of the paint by almost one hundred per cent.

The problem of preserving a complicated steel structure such as a bridge can be materially aided by proper design considerations. With faulty design a number of maintenance difficulties may be created. Unless drainage points are provided, rain-water and dust may collect in pockets and greatly shorten the life of the coating at those points. Sharp recesses are difficult to paint, with the attendant danger of having little or no protection given to them. In most cases, such faults of design can be corrected without altering seriously either the strength or the cost of the structure. Attention should also be paid to the facility with which scaffolding for future repainting may be erected.[1] A little more care and attention at the blueprint stage of a structure may pay large dividends in future economy of maintenance.

Probably the most important single factor which determines the life of a protective paint coating on steel structures is the surface preparation of the metal. It is generally agreed that a thoroughly cleaned surface, that is, one completely free of rust, scale, grease, etc., furnishes the best base material upon which to apply a protective paint. In actual practice, however, this ideal condition can only rarely be obtained and hence the practical problem usually becomes one of striking a suitable compromise.

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[1] Adrian, *Farben Ztg.*, 39, 1146, 1170 (1934), offers a number of practical suggestions on design.

For new structures, not as yet erected, it may be profitable to consider surface preparation and priming at the steel mill where the structural iron parts are fabricated. At the mill the problem of complete scale removal and controlled application of the inhibitive priming coat is a relatively simple matter. In this connection, a method of mill-priming, recently recommended,[2] is of particular significance. The method of pickling which is suggested appears to be both economical and efficient. This method, which is described in Chapter 2, makes use of sulfuric acid for removal of the scale followed by a final pickle in phosphoric acid to produce an improved surface for the retained adherence of the paint coating, which is applied to the structural members immediately after pickling while the dry parts are still warm. It is pointed out that such structures primed with a red lead paint, for example, are able to withstand considerable abuse during handling prior to erection. In actual industrial applications, this method of mill-priming has so far given excellent performance records, the adhesion of the priming coat with its attendant absence of corrosion being remarkable. Storage tanks pickled by this process over 5 years ago showed that the priming coats are still elastic and the steel completely free of corrosion, whereas other tanks erected at the same time without a pickling treatment showed definite rusting all over within two years after painting.

The more common practice of preparing a structure for painting is to perform the cleaning operations on the structure after erection. It is here that the difficulty of striking the best compromise on practical cleaning methods is encountered, since both rust and scale should be removed as far as it is economically feasible to do so. The problem of removing rust is not as difficult as that of removing scale, and both mechanical and chemical methods are effective for this purpose. Of chemical methods, the practice of washing with dilute aqueous solutions containing phosphoric acid, alcohol or other water-miscible organic solvents and an inhibitor is finding increasing adoption. Such washes serve to convert the rust to a relatively harmless and well-anchored phosphate. Mechanical methods, such as wire brushing, sandpapering, etc., by hand or machine, and sand or shotblasting, are also effective means of removing rust.

The removal of scale presents a problem of long standing, which as yet has not been completely solved with respect to its economic aspects. The details of several methods of removing scale have been discussed in Chapter 2. With respect to the paint problem, the difficulty arises from the fact that partial scale removal is definitely inferior to complete scale removal, but the latter is difficult and costly to realize on erected structures.

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[2] Footner, H. B., *Fifth Report of the Corrosion Committee of the Iron and Steel Institute (London)*, p. 369, 1938.

One method, which has been used to a considerable extent, particularly in the ship-building industry, is to permit the iron and steel surfaces to weather for appreciable periods (six months to a year), during which time the scale becomes loosened by under-rusting and is readily removed by wire brushes, hammers and chisels. The problem has been altered from the difficult one of scale removal to the less difficult one of rust removal. Recent studies on improvement of wire brushes [3] hold out promise that this method may become effective in removing even the most adherent scale. At present, the best means of removing scale is to blast the metal surface with sand, steel shot or steel grit. With the use of sand the necessary precautions must be taken against silicosis, and with steel shot or grit the operation must be designed to conserve the relatively expensive abrasive, limiting the use of this material to descaling of structural parts before erection.

It is difficult to obtain reliable relative costs of these various cleaning operations. Labor costs, accessibility, amount of scale, etc., all affect the cost and are hardly ever comparable. Recently cost studies have been conducted on the various descaling methods and have shown a surprisingly low relative cost for sand and shotblasting methods.[4] These costs have been computed in terms of cost per square foot and are reproduced in Table 43, from the Fifth Report of the Corrosion Committee,[3] (page 352).

Table 43.—Costs of Mechanical Descaling Processes.[1]

Computed from data given by Kappler, F., *Zeitschrift des Vereines deutscher Ingenieure,* 80, 781 (1936).

	Cost in Pence per Square Foot		
Descaling Processes	A. Old Painted Steelwork on the Site	B. New Rusty Steelwork in the Shop	C. Smooth Sheets in the Shop
Hand brushing	9.5	1.67	0.42
Mechanical brushing	5.4	1.26	0.32
Pneumatic chisel	6.8	2.44	0.97
Sandblasting (hand-operated)	4.8	1.03	0.29
Shotblasting (hand-operated)	...	1.03	0.29
Sandblasting (mechanical)	...	...	0.32
Shotblasting (mechanical)	...	...	0.32
Shot slinging	...	...	0.39

1. These are net costs and do not include administrative overheads and profits. They are calculated on the following assumptions:

(a) Labor costs are 1s. 3d. per hr. for band cleaning and 1s. 6d. per hr. for other operations.

(b) The cost of quartz sand is 30s. and that of steel shot £14 per ton.

(c) The cost of compressed air has been calculated on the basis of 18 h.p. per 138 cu. ft. per min., electrical energy being reckoned at ½d. per Kwh. The depreciation on the actual compressing plant has been taken as being covered by the sundry costs included in the author's original table. It is not clear whether this is a permissible assumption.

At present the normal commercial practice of scale removal consists essentially of the removal of surface products which yield to the scrubbing action of a wire brush, usually manually operated. With such incomplete scale removal, the practice of employing a wash containing phosphoric acid and an inhibitor unquestionably aids in reducing the local corrosion potentials set up at the scale-iron boundaries. The further incorporation of a good inhibitive pigment, such as red lead, zinc chromate, etc., in the priming coat, adds a second line of defense against the corrosion hazard introduced by partial scale removal. It is probably safe to say that at the present time there is still insufficient information to prescribe unequivocal instructions as to the best cleaning practice that might be followed under all practical conditions.

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[3] *Fifth Report of Corrosion Committee of Iron and Steel Institute,* p. 355, 1938.

[4] Kappler, F., *Zeitschrift des Vereines deutscher Ingenieure,* 80, 781 (1936).

Even with the most effective surface cleaning methods, certain other precautions must be followed if a durable paint coating is to be expected. It is well recognized that paints should be applied only to dry surfaces. Painting either during rain or immediately thereafter is obviously undesirable. Furthermore, in humid, cool climates, painting on any given day is best delayed until the high humidity incident to early morning conditions has subsided. In order to minimize the deleterious effect of thin condensed moisture films, the practice of preheating the work by a blow torch or by burning off a brush coat of organic solvent has been at times resorted to and beneficial results have been reported. Painting at temperatures below 40° F. is generally not recommended. In Germany a special hot spray procedure has been developed[5] which is finding increasing use. This hot spray application is essentially a modern version of the old encaustic process and is approximately as follows. A paint vehicle consisting of a thick, highly-bodied drying oil mixed with wax and suitable pigments is electrically heated in the cup of a spray gun. The spray is hurled out into a flame which serves the double function of drying and heating the surface, as well as preventing solidification of the spray particles. In this method of application a greater degree of independence from immediate weather conditions is attained. Satisfactory performance of coatings applied in this manner is reported.

Normally, protective paints for metals are applied to structures *in situ* by brush. This permits a certain amount of working of the priming coats into the incompletely cleaned surface. Relatively inaccessible regions can be brush-coated which might be partially shielded in a spray application. However, on large and relatively well cleaned surfaces, the use of a spray gun proves both economical and effective. In laboratory studies, no inherent differences have been found in the durability of paint systems applied by brush or spray gun on clean surfaces under controlled conditions.

It is good practice to permit as much time for drying between coats as is economically feasible. In the case of large structures, this is frequently not a difficult objective to meet. Certain weather conditions, such as high winds, accompanied with appreciable quantities of dust, are distinctly deleterious, owing to the embedding of numerous foreign particles in the film. Each of these particles potentially sets up a definite point of weakness. The recent practice of modifying the composition of the paint vehicle in the direction of more rapid drying, so that its susceptibility to weather conditions is reduced, will probably prove important in practice.

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[5] Adrian, *Farben Ztg.*, 39, 869 (1934).

For exterior metal protective paints, linseed oil base vehicles are most commonly used. A number of studies have shown that differences in durability, obtained with linseed oil of different sources, are of a negligible order, provided the oil has been sufficiently refined to remove most of the foots and mucilaginous matter. More recently, the question of the comparative value of partially polymerized drying oils, or suitably resin-reinforced linseed oil has been extensively studied, and it is perhaps as yet too early to draw final conclusions as to relative merits of these paint media. In general they appear to offer certain advantages over ordinary linseed oil. As pointed out in Chapter 13, the benefits conferred by speedier drying or by the development of toughened and less permeable films can be offset by such a sacrifice in long-range durability as to make the more immediate benefits questionable. Future work will undoubtedly aid in clearing up this question.

By way of general guidance, the following paints are suggested for assuring satisfactory performance on steel structures. In making such recommendations it should be kept in mind that no attempt at completeness is intended. Unquestionably, any list of recommended paints for purposes of rust protection is open to criticism for its sins of omission, as well as of commission. With such reservations, priming paints for steel structures containing the following pigments or pigment combinations may be suggested: red lead, iron oxide containing either about 25 per cent zinc chromate or 4 to 16 per cent zinc oxide, basic lead chromate, zinc dust-zinc oxide, and metallic lead pigments. In addition to these, favorable reports have appeared in the literature upon the use of basic carbonate white lead, sublimed blue lead, and ammoniated charcoal pigments. Of these various priming pigments, red lead of the 90- to 95-per cent Pb_3O_4 grade has enjoyed widest use and the most consistently favorable results. The incorporation of approximately 25 per cent zinc chromate with either inert or mildly basic pigment combinations also finds wide favor. In such a paint the incorporation of a basic pigment, such as zinc oxide, aids in overcoming its weakness in an acidic environment.

In using these paints, whether for priming or top coats, care should be exercised to utilize a pigment-vehicle ratio which is optimum both for purposes of application and for durability. For top coats a larger number of paints have given satisfactory performance. Typical of these are the following: iron oxide (calcium sulphate-free), graphite, leaded zinc oxide, micaceous iron oxide, lead titanate and other titanium pigments, white lead, and aluminum powder. Various combinations of these pigments are used both for satisfying appearance requirements and for improving durability. From the standpoint of protection, the chief purpose of a top coat is to protect the priming coat for the longest possible time.

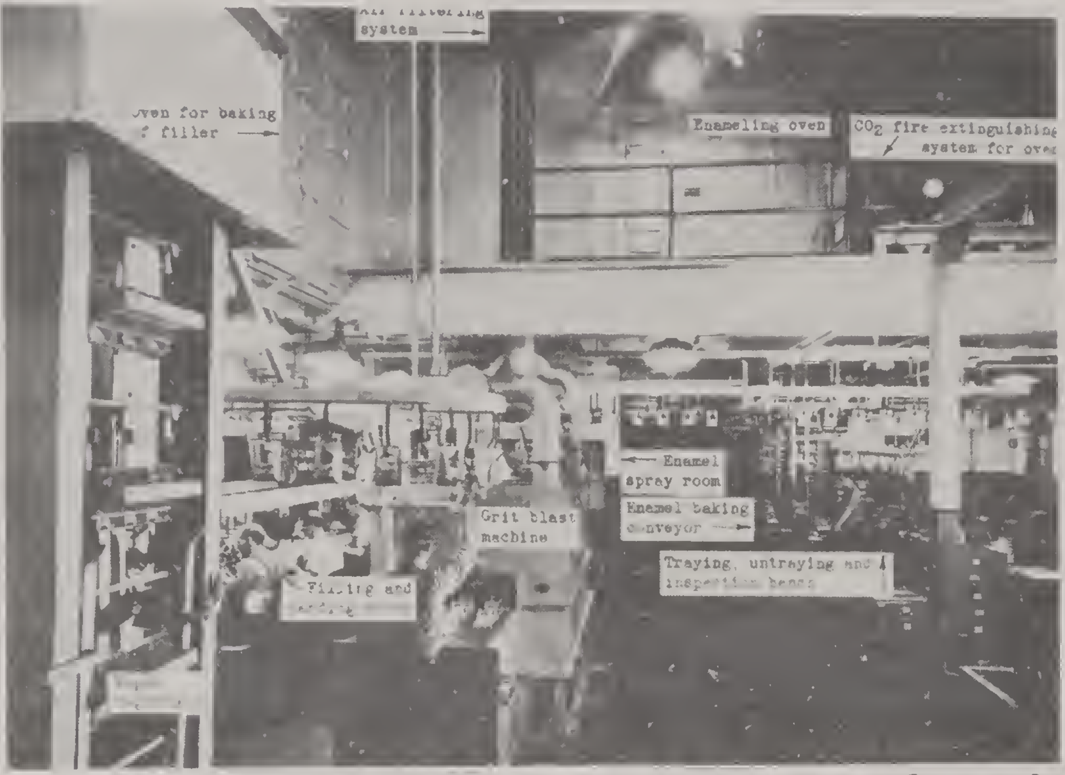
With regard to the maintenance of paint coatings, it is generally agreed that the most economical practice is to repaint before the priming coats are dangerously attacked, inasmuch as the expensive problem of reconditioning rusted areas is thus avoided. Many of the large companies have adopted the practice of frequent inspection of their painted structures, and an experienced inspector can usually tell without much difficulty when repainting is advisable. The frequency at which such structures must be repainted varies considerably, depending on a number of factors, such as the quality of the previous painting and the severity of exposure. In general, it may be said that actual paint applications on structures do not show the life promised by panel exposure tests with the same paints. Four- to six-year life on inland rural exposures at latitudes above 40 degrees may be considered as good average performance for a three-coat application. In industrial areas this normal life expectancy may be shortened to about 3 to 5 years. In coastal regions a life of 3 to 6 years may be expected, depending on the proximity to additional pollution from industrial regions. It must be clearly recognized that such life expectancies carry large elements of chance owing to the many factors involved. Unquestionably, unusual records of individual experiences can be cited in which a performance life considerably beyond these limits is found. It is safe to predict that, as a consequence of the many paint studies currently engaged in, the average life of actual practical paint jobs will be considerably extended in the future.

Painting of Industrial Equipment

The problem of finishing industrial equipment is in several respects quite unlike that of painting large immobile structures, exposed either to the atmosphere or buried in the ground. Both the type of finishing materials used and their method of application is essentially different. The organic coatings designed for equipment, in addition to offering corrosion protection for the underlying metal, usually must meet definite appearance requirements, both initially and for protracted periods of time, and must offer considerable resistance to mechanical stresses of various kinds. Consequently, the enamel types of coating, *e.g.*, a nitrocellulose base, a baking varnish, or an oil-modified synthetic resin, find almost exclusive use for painting equipment, such as automobiles, electrical apparatus, office equipment, cash registers, household refrigerators, etc.

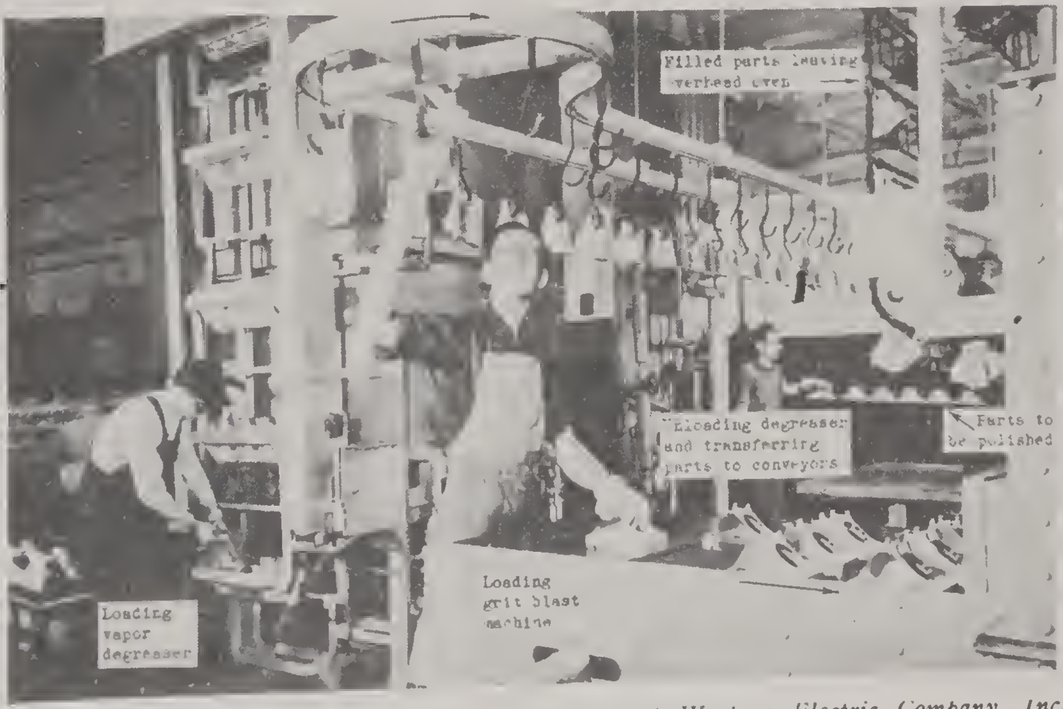
Such equipment is finished indoors under modern, high-speed manufacturing conditions. Wherever feasible, that is, where production schedules are sufficiently high, the various process steps used in applying these finishes, such as cleaning, surface treatment, application of the coating, drying or baking, are placed on a mechanical basis. To make this possible, conversion of the finishing medium to a hard, tough coating must be rapid; consequently the exterior type of paint coating finds practically no application, since it dries much too slowly and offers insufficient resistance to the mechanical abuse incident to assembly and transport of such equipment.

The procedure used in finishing different types of equipment requires methods that may vary considerably, depending on the kind of metal used, its history of fabrication up to the point of finishing, and the kind of organic



Courtesy of Western Electric Company, Inc.

Figure 78.—Finishing Telephone Handset Bases, General View.

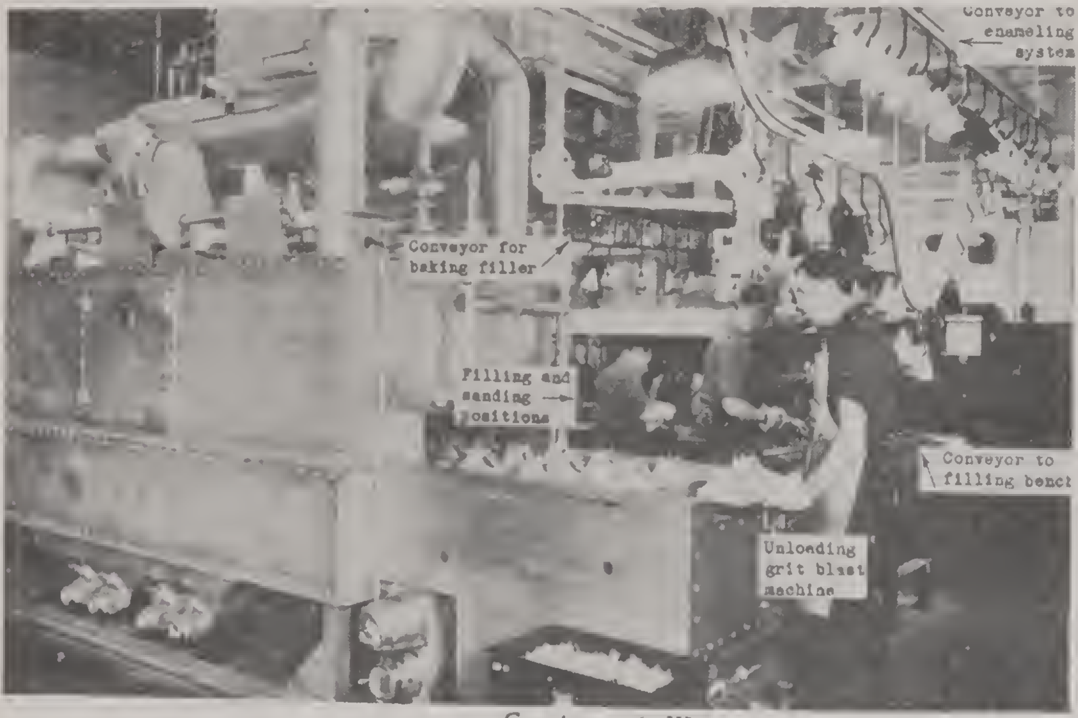


Courtesy of Western Electric Company, Inc.

Figure 79.—Finishing Telephone Handset Bases. Start of Finishing Operations: Degreasing, Polishing and Grit Blasting.

protection desired from the standpoint of serviceability and life. In general, the finishing operations are brought to a high order of control and the importance of thorough preparation of the metal surface before painting is fully realized and acted on. By way of illustration, the current finishing practices used in the manufacture of two entirely unrelated items of equipment, namely telephone handset bases and passenger automobiles, are described in some detail.

Telephone handset bases, manufactured by the Western Electric Company, are at present die-cast from a zinc alloy and are finished with a black synthetic resin type of baking varnish, which is formulated to match the appearance of the phenol-plastic handset associated with it. The organic finish must protect the underlying metal against corrosion and maintain a sightly appearance for many years of service. The operations involved in the production of this high quality finish are approximately as follows (Figure 78).

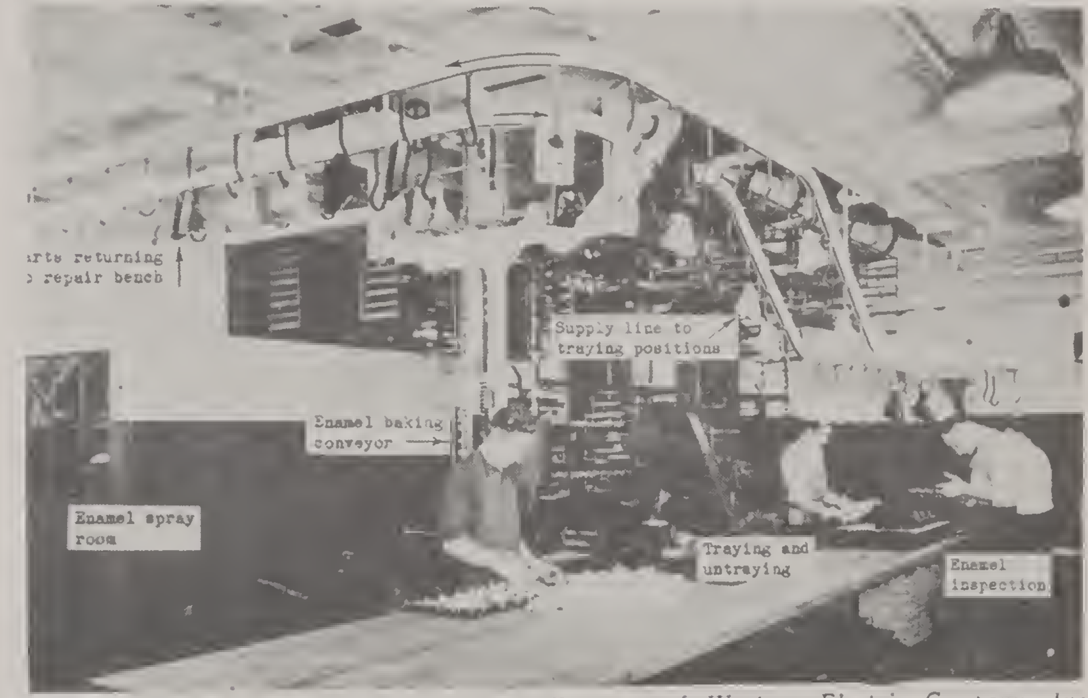

Conveyor to enameling system
Conveyor for baking filler
Filling and sanding positions
Conveyor to filling benc
Unloading grit blast machine

Courtesy of Western Electric Company, Inc.

Figure 80.—Finishing Telephone Handset Bases. Completion of Surface Preparation: Grit Blasting, Filling and Sanding.

The die-cast bases are placed in the carriers of an automatic solvent vapor degreasing machine to remove residual oil from machining operations. The parts are then placed on an overhead monorail conveyor which delivers them to the loading end of a straight-line grit blasting machine (Figure 79). Steel grit is used instead of sand, as it produces a more suitable surface for the enamel coats and simultaneously eliminates the silicosis hazard. At the discharge end of this specially-designed blasting machine, excess steel grit is removed by the use of compressed air. Some sorting of parts may be necessary at this point for filling of casting imperfections, the filled parts being subjected to a short baking operation in which automatic conveyors are used and the excess filler is sanded smooth (Figure 80). All parts, filled or unfilled, are brushed thoroughly to remove grit and dirt, hung on another overhead monorail conveyor and delivered to the racking bench (Figure 81).

At this point the bases are placed on specially designed spray fixtures and placed on the carriers of a conveyor type oven which transports them to the spray room. This room is equipped with centrifugal type water-washed spray booths (Figure 82), the water-wash minimizing the work of cleaning the booths and reducing fire hazards, inasmuch as all paint residues are washed down, emulsified, and collected in sludge tanks outside the booth. Fresh air is supplied at a slight outward pressure to this enclosed spray room through a self-cleaning oiled-curtain type of air filter. Spraying is performed manually and each operator is equipped with a spray gun supplied with uniform air and paint pressure, through a central paint distribution system located in a special fire-proof room. The sprayed work is then transported by carriers on a continuous chain conveyor through a baking oven, heated by an indirect gas-fired heating system, the air in the oven being filtered. The bake ovens are equipped with accurate temperature control and regulating devices and for precaution against fire an automatic carbon dioxide fire extinguishing system is provided (Figure 83). After receiving two coats of enamel, each of which is baked for one hour

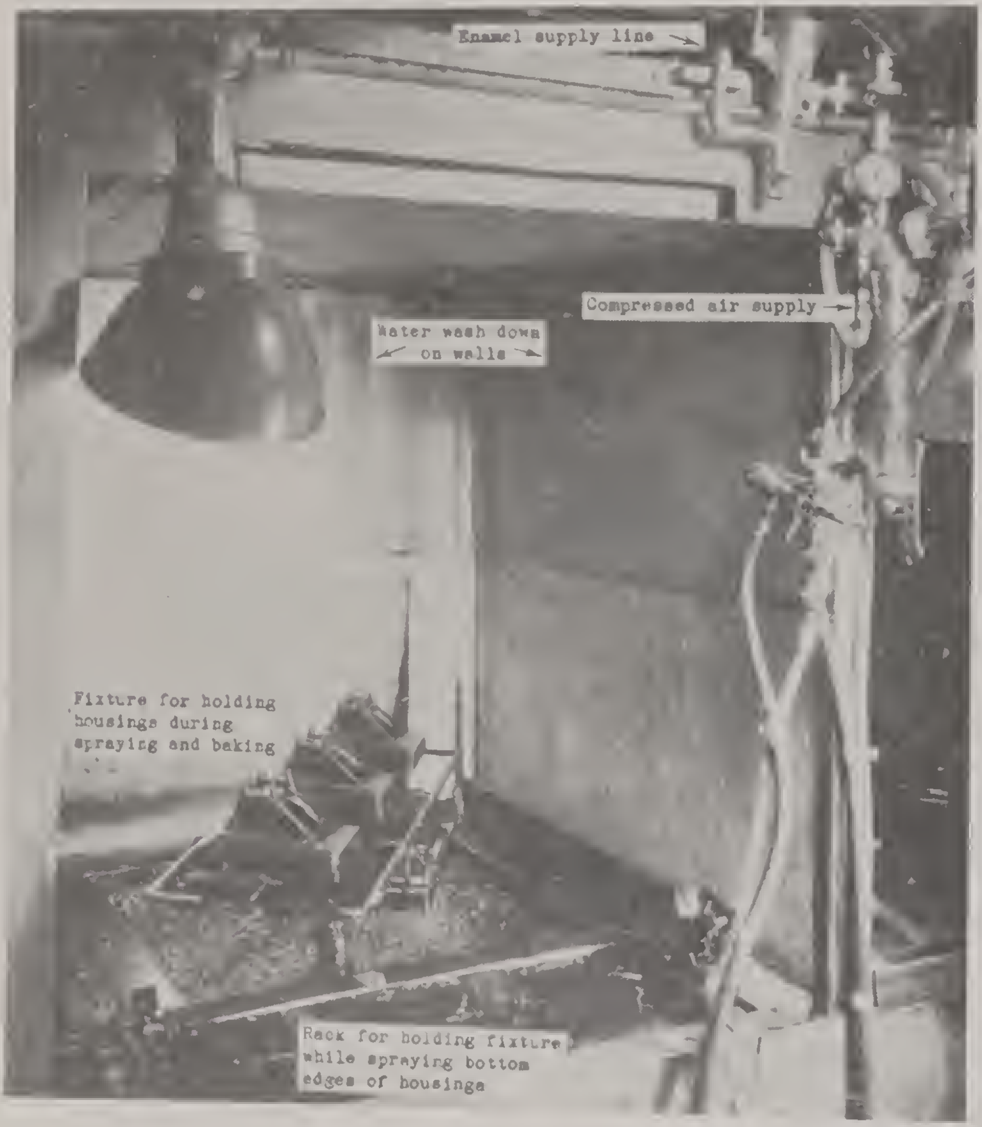


Courtesy of Western Electric Company, Inc.

Figure 81.—Finishing Telephone Handset Bases. Beginning and End of Enameling Process: Traying, Untraying and Inspection of Parts.

at 350° F., the finished parts are inspected for appearance and conformance to rigid standards, as required in process specifications.

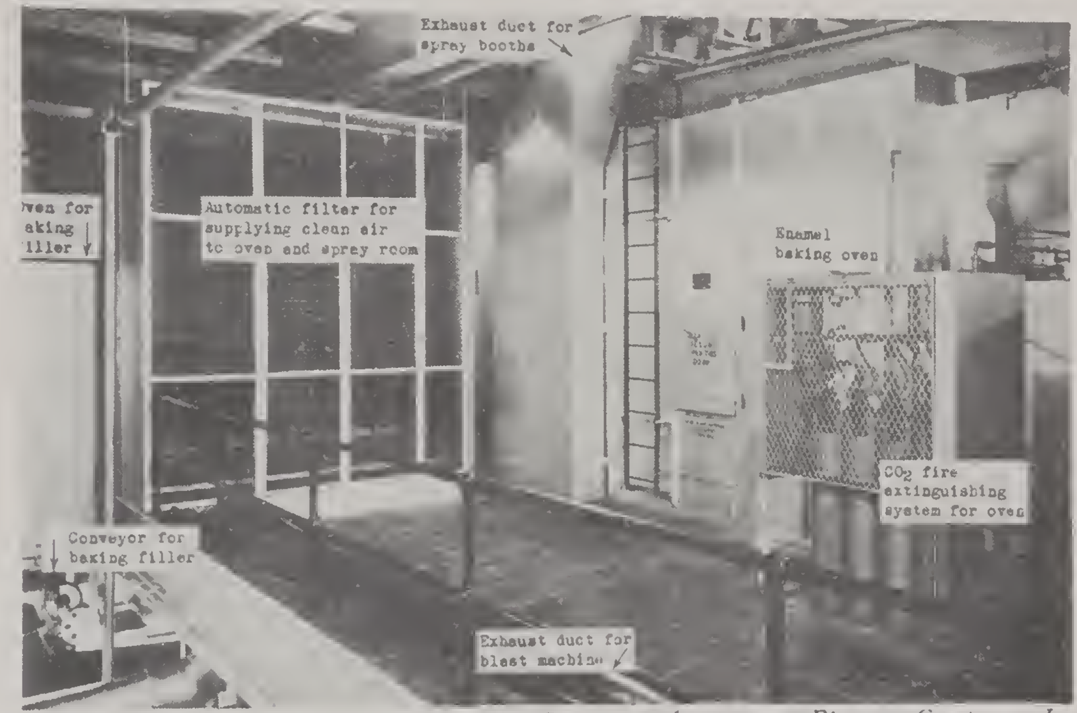
A finish such as this is able to resist severe mechanical abuse without separating from the base metal, and it satisfactorily withstands exposure outdoors or in high humidity for a period of several years. The absence of a corrosion-inhibitive priming coat is in marked contrast to the practice of finishing metals designed for outdoor exposure. The high quality of such a finish is attributable to a combination of factors such as careful selection of the finishing medium, thorough surface cleaning and preparation, and a high degree of control of the spraying and baking operations.


Enamel supply line
Compressed air supply
Water wash down on walls
Fixture for holding housings during spraying and baking
Rack for holding fixture while spraying bottom edges of housings

Courtesy of Western Electric Company, Inc.

Figure 82.—Finishing Telephone Handset Bases. Parts Mounted for Spraying.

The finishes of passenger automobiles have been brought to a very high level of quality during the last few years. Owing to large production schedules, practically every step in the sequence of finishing operations has been placed on a conveyorized basis and the element of time constitutes perhaps the most important economic factor. Before the advent of nitrocellulose lacquers, the finishing of an automobile was an operation consuming several weeks; and unfortunately the time required in service for unsightly surface cracks to appear was also a matter of weeks. At present, finishing schedules are figured in terms of hours and service in years. In fact an eligible finishing material for this industry is considered unsatisfactory, if within two years' exposure to the Florida sun, test panels should chalk to a point where the original gloss cannot be readily restored by a polishing operation.


Exhaust duct for spray booths
ven for aking iller
Automatic filter for supplying clean air to oven and spray room
Enamel baking oven
CO2 fire extinguishing system for oven
Conveyor for baking filler
Exhaust duct for blast machine

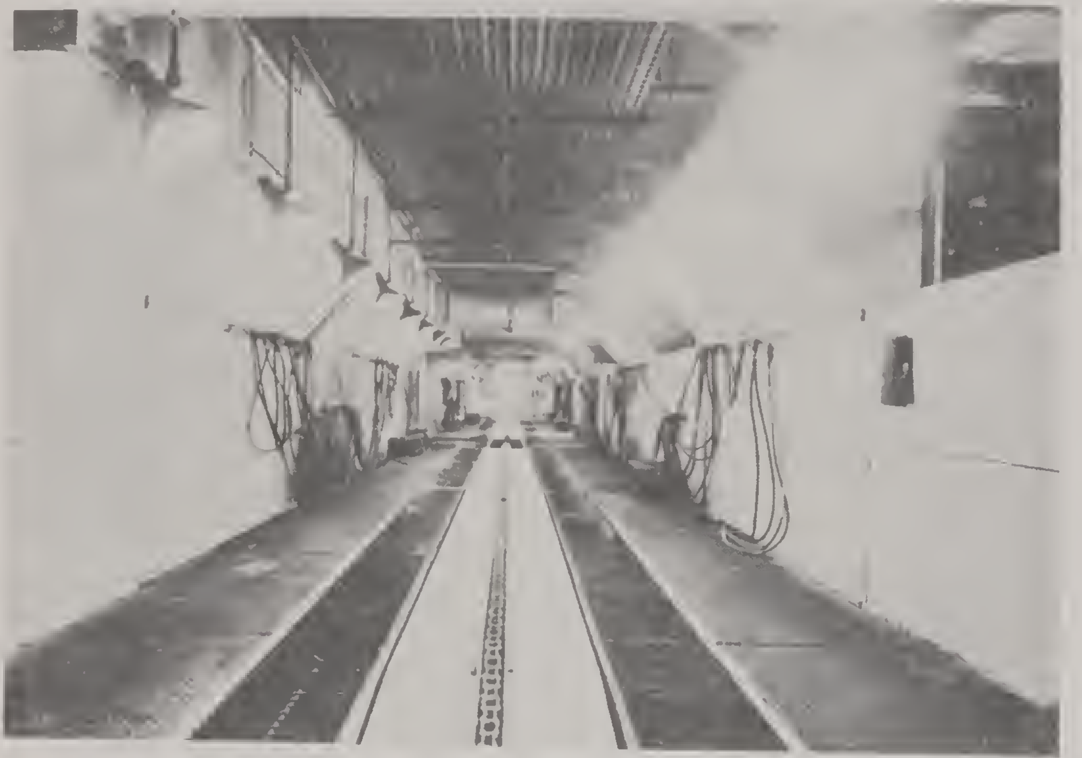
Courtesy of Western Electric Company, Inc.

Figure 83.—Finishing Telephone Handset Bases.
Oven and Associated Equipment.

At present, two general methods of finishing passenger vehicles are in use. One consists of a system in which the color coats are of a nitrocellulose enamel nature, whereas in the other the top coats consist of baked oil-modified synthetic resin enamels. The following is a schedule of the process steps involved in the finishing of automobiles in which nitrocellulose enamels are employed:

Cleaning.—A preliminary air blast is used for removing gross dirt, filings, loose solder drips, etc. The body is next washed off with a hot-water solution containing both alcohol and phosphoric acid to remove superficial rust and oil films. It is next scrubbed with oleum spirits by means of brushes. This is followed by a hot-water rinse. At times susceptible areas, where moisture may become entrapped, are given quick phosphate treatment for local rust-preventing purposes. Recently, some of the manufacturers have adopted the practice of phosphating the entire body to obtain improved adherence of the finish. The body is then dried in a hot oven and blown off with air at points where water may have collected. Immediately before the application of a sprayed coating, the entire body is rubbed off with special rags, impregnated with a resin medium in a tacky stage, for the purpose of picking up chance dust particles. This operation is called "tack-ragging."

Priming.—The priming coat is now sprayed on. Usually an oil base material, containing iron oxide as the principal pigment, is used. Great care is exercised in the spray booths used in the automobile plants to prevent dust from falling on the surface. The air in the booths is filtered and maintained at a slight outward pressure to prevent dust from being sucked in. In addition, the walls of the spray booths are coated with a dust-trapping film frequently consisting of a sticky medium such as castor oil. Large volumes of air are employed and the suction is usually applied at the floor level (Figure 84), owing to the greater density of the vapors released.



Courtesy of R. C. Mahon Company

Figure 84.—Tunnel Spray Booths for Continuous Automobile Painting. Down-draft Hydro-filter spray booths in a line for continuous automobile body finishing. Filtered air enters through the perforated ceiling and fumes are carried off through vents near floor.

The priming coat is then baked about one hour at approximately 200° F. After this, a surfacer coat is applied which is similar in composition to the priming coat, except that somewhat more pigment is incorporated in the vehicle to facilitate ease of sanding. This surfacer coat receives a bake similar to that of the priming coat. The combined primer and surfacer are then sanded. For the automobile industry, special sandpapers have been developed to permit rapid sanding under a constant stream of water. This sanding operation is usually conducted by hand, although for certain areas on the body special machines have been developed.

After sanding, local imperfections, such as dents, mars, deep scratches, etc., are filled with what is called a glazing putty, usually of a pyroxylin base. This dries quickly and is sanded off locally to conform to the rest of the surface.

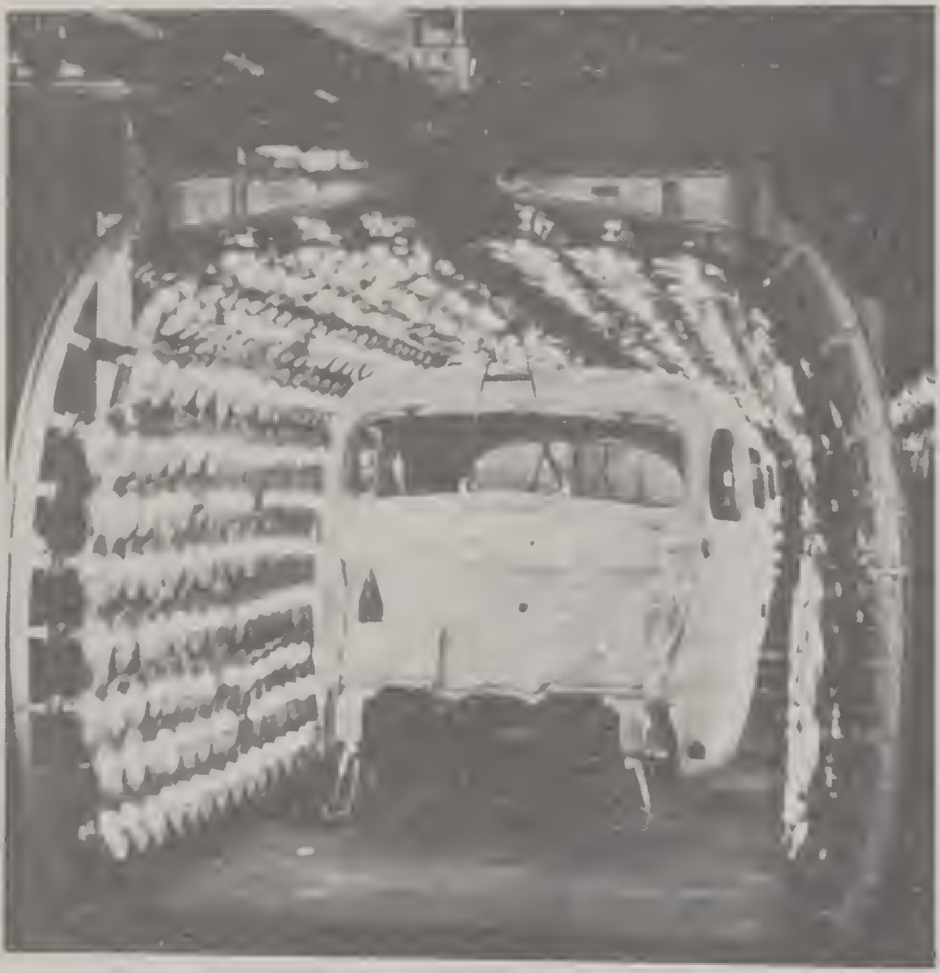
Finish Coats.—Two coats of the appropriate colored pyroxylin enamel are then sprayed on and given a short dry to expedite escape of solvent (5 minutes at 150° F.). This is followed by two more spray coats, and the entire system is then dried for approximately 20 minutes at 180° F. The last coat is subjected to a final polishing operation. This is usually done by means of a power-driven rotating disc of lamb's wool and a polishing abrasive, consisting usually of a mixture of a finely divided soft abrasive, such as rotten stone, in a waxy vehicle.

Sheet-Metal Work.—The sheet metal parts, such as hoods, fenders, running boards, gas tank, covers, etc., are treated slightly differently. In most automobile plants the cleaning and surface preparation of these parts is performed on automatic conveyors as follows: Dip in boiling hot dilute alkali cleaner for grease removal, followed by thorough rinsing in hot water. This is followed by a rapid phosphating treatment either in dip tanks or in spray booths (see Figure 89). Usually such a treatment is followed by a dip in a hot-water solution containing a small amount of chromic acid for additional inhibitive purposes. This last dip is allowed to dry in suitable ovens without further rinsing.

For black fenders, black Japan is applied by dipping and is then baked for 30 minutes at 450° F., and then followed by a second dip and a similar bake. For colored fenders, defective black japanned fenders may be sanded, after which the pyroxylin color coat is applied. In other cases, an oil type primer baked at 300 to 350° F. for 30 minutes may be used; this is then sanded and followed by 2 or 3 coats of the pyroxylin color enamel. On hoods and other sheet-metal parts, baking gray primers followed by lacquers are frequently used.

When baked synthetic resin-varnish finishes are used for top coats, the process leading up to the top coats is essentially the same. Owing to the greater solids content of these enamels as compared with nitrocellulose enamels, two coats of these baking materials usually give a film thickness equivalent to that obtained with four coats of nitrocellulose enamels. After the priming and surfacing coats, the first color coat is sprayed on, and is then baked usually for about one hour at approximately 250° F., or for a shorter period of time at a somewhat higher temperature. This coat is then wet-sanded, dried and tack-ragged, after which the second and final color coat is applied and given a similar baking treatment.

With the use of these baked synthetic finishes, more care must be exercised to prevent local marring of the finish, owing to the greater difficulty of repairing such defects. The Ford Company has developed a rather novel method of making these local repairs. In the neighborhood of a scratch the finish is lightly sanded to promote the adherence of the sprayed repair patch, which is baked by the use of specially designed lamps. A lamp of the carbon-filament type, normally used for therapeutic purposes, is fitted with a gold-surfaced reflector and is held approximately 12 to 20 inches away from the surface; the finish is baked in a matter of minutes. This method of baking is now used extensively at the Ford River Rouge plant for other operations in addition to repair work. For instance, the priming coat is baked in a novel arrangement in which the conveyorized body is surrounded by a clam-shell arrangement on which a large number of these lamps are suitably placed (Figure 85). The two halves of the clam-shell ride parallel to the body for a period of about seven minutes, after which they are returned to surround another body coming along on



Courtesy of Ford Motor Company

Figure 85.—Baking Finish on Automobile Bodies. In some cases synthetic enamel finishing coats on automobile bodies are baked by means of therapeutic lamps arranged in banks.

the conveyor. It is stated [6] that this seven-minute bake is approximately equivalent to the usual one-hour bake. Similar tunnel ovens employing these carbon lamps are used for drying off rinse water before baking and other heating operations.

In the use of either nitrocellulose or synthetic resin enamels, care is exercised in the proper balance of the solvents, so that a high-gloss, well-knit film is at all times produced. Considerable development has been necessary in the selection of optimum pigment combinations and the difficult problem of color matching between parts finished at different points in the factory has been successfully overcome. There is a difference of opinion as to whether the synthetic resin type of enamel is superior to the nitrocellulose enamel. Advances have been made in both classes of materials and it may be said that each class, when properly formulated and applied, yields finishes with remarkable performance records indeed. It may be of interest to know that the finishing schedules of low and high priced cars are practically the same. Essentially, the difference between them lies in the closer attention paid to perfection of finish appearance in the more expensive cars, The additional rubbing, polishing and inspecting required to produce this order of perfection is relatively expensive, but adds little of intrinsic value to the serviceability and life of the finish.

Protection of Underground Pipe [7]

It was estimated [8] in 1931 that there were exposed in the soils of this country close to 500,000 miles of pipe lines and 27,000,000 house service connections. The value of these pipe systems was estimated at more than $5,000,000,000, and the annual loss due to corrosion close to $150,000,000. In considering the problem of diminishing these losses, a number of factors are found to have a bearing on the economics of this situation.

From a technical standpoint the problem of protecting underground pipe against corrosion is in many respects dissimilar to that encountered in the protection of iron and steel against atmospheric corrosion. There is first of all the consideration of the type of underground pipe distribution system, that is, whether it is a metropolitan low-pressure gas or water system, or a trunk-line system carrying gas or oil at high pressures over long distances. The methods of protecting the two kinds of systems are different in a number of respects. There is the question of the physical and chemical constitution of the soil in which the pipe system is buried. In most instances these soil factors are of more importance in controlling corrosion of pipes than the particular kind of ferrous metal of which a pipe is made. This requires, particularly in the case of long pipe lines, a thorough knowledge of the soil, for it is found that in some soils no protection of the pipe may be needed, whereas in other highly-corrosive soils, the best protection available is indispensable. As a rule, pipe buried in the ground requires protection against corrosion, and the coatings employed for this purpose are usually very much thicker than the organic coatings used for atmospheric exposure. Such coatings must also be able to resist stresses of various kinds, such as impact during the laying of the pipe and the long-time soil stresses associated with changes in water content and motion of the soil. More recently the practice of cathodic protection to buried pipe is coming into increasing use, both as a means of protection against stray electrical currents produced by external electric fields, and currents due to the operation of galvanic cells on the pipe itself.[9] This is accomplished by raising the potential of the surrounding earth by means of a storage battery, D. C.-power supply, or by the use of a highly electronegative metal such as zinc.[10] The usual arrangement is to bury a metal electrode in the soil at a certain distance from the pipe to be protected and to attach the positive pole of the battery or the power lead to this metal. When zinc is employed, it may be used in the form of bars or wire; in the latter case it may be buried in parallel with the pipe and attached by an insulated lead to the pipe at suitable distances. The current required to prevent corrosion of coated pipes (at defects in the coating) is usually much less than that necessary to protect bare pipe. It has been used most successfully on single pipe lines in areas in which other pipe lines are not involved.

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[6] McCloud, J. L., *S.A.E. Journal, Transactions*, 42, 131 (1938).

[7] Ewing, S., "Soil Corrosion and Pipe Line Protection," American Gas Association, New York, 1938.

[8] Shepard, E. R., *Gas Age Record*, 68, 333 (1931).

The soils of this country have been carefully mapped and classified. Such classifications are primarily based on the geologic history of an area and the manner in which the soil has been modified by the average climate over a large number of years. In the far mid-west, that is, in the arid and semi-arid belt, the soils are relatively unleached and hence high in soluble alkalies. Owing to the scarcity of water, such a region is usually non-corrosive to pipe except in such localities where water may collect at times, in which case they may become quite corrosive. Eastward from this arid region the amount of annual precipitation is larger and an appreciable quantity of soluble alkali has been leached out. However, the soil is still alkaline and owing to the greater amount of water normally in the ground, corrosion of buried pipe is frequently more widespread in this area. Other parts of the country, such as the northeastern section, are in general characterized by acidic soils. This territory is geologically older and therefore better leached and the gradual accumulation of humus matter has shifted the soil to an acidic condition. The eastern seacoast area, as well as the general southeast section of the country, are characterized by sandy soils. If these are well drained, they constitute, as a class, the least corrosive soils for pipe burial and at times permit the safe burial of bare pipe. With respect to soils in general, it may be said that the combination of poor drainage and high electrolyte content makes for rapid corrosion, whereas the combination of good drainage and low electrolyte content makes for little corrosion.

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[9] Kuhn, R. J., *Proc. Am. Petroleum Inst.* 14, 153 (1933); Bridge, A. F., *Natural Gas*, (Dec., 1934); Smith, A. V., *Proc. Am. Gas Assoc.*, 19th Annual meeting, p. 816 (1937).

[10] Rhodes, G. I., *Proc. Am. Petroleum Inst.*, 17, 21 (1936).

The importance of variations in the soil depends to a large extent on the kind of pipe line to be buried. Thus, in the case of long lines extending over several hundred miles, in which there is a considerable economic stake involved, it has become customary to survey the terrain in which such a pipe is to be laid. The experienced soil expert is thus enabled many times to avoid or warn against dangerous stretches such as river crossings, local swamps, etc., and in many instances, such "hot spots" can be avoided without additional expense.

A technology of soil testing has been developed in which a number of factors are examined for their relation to the corrosiveness of the soil. Such soil test methods have not always been completely successful owing to the many variables involved. It is customary to determine the pH value of soil extracts, the conductivity of the soils, and the nature of the electrolytes furnishing the ions for this conductivity. In addition to these factors, the relative ease with which the electrolytes, as well as gases, can migrate in the soil is important, and this depends to a large extent on the texture of the soil, that is, the size and distribution of the soil particles. The National Bureau of Standards has critically studied a large number of soils and has selected 47 different burial locations, characterized by distinct differences in respect to one or two of the above factors, for its test burial sites of thousands of test specimens. Denison[11] has developed a laboratory soil test which offers one of the best means so far available of quickly gauging relative soil corrosivity. This is described in Chapter 12. Until more is learned of the relations of depth of pitting and time of exposure, the most effective means of getting information relative to the probable life of pipe buried in the ground is still by the hard road of experience. Several of the larger pipe users keep complete records of failures, which are charted on suitable maps. By this means, in the course of years a reliable picture of the relative corrosiveness of soils in various parts of an area is obtained and proper action with respect to the laying of new pipe or pipe replacements is made possible.

Hundreds of different coating materials have been tried at various times as a means of minimizing the corrosion of buried pipe. Paints of many kinds, lacquers, bituminous materials of either asphaltic or coal tar origin, metallic coatings, vitreous enamels, greases and cements may be mentioned. Of these, not one has given perfect protection in all soils, and yet unquestionably the better ones have served to prolong the life of pipe lines for many years in corrosive locations. The type of coating to be selected is to a large extent dependent on the type of pipe line to be protected. In the case of urban pipe systems, which are usually made up of a considerable network of relatively small pipe, it is generally considered more economical to buy protection in the form of heavier pipe wall section, such as is typical of cast-iron pipe. In a city water or gas system, the number of connections to be made, the frequency of digging up trenches, and the use of low pressures have usually dictated the use of this type of pipe. In long trunk pipe lines, however, it is customary to use steel pipes, owing to the greater pressures involved, and the high cost of transporting heavy wall, large diameter pipe. It is in this class of pipe lines where the greatest advance in the technology of pipe coatings has been made within the last ten years.

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[11] Denison, I. A., *J. Research Nat. Bur. of Standards*, **17**, 363 (1936).

It is a matter of considerable difficulty at the present state of development to attempt to set up specifications which would insure a definite pipe life. The variables that enter are numerous, and standardization, as well as control, of practices, particularly in the field of protective coatings, is in need of further development. There are, however, certain important facts concerning pipe coatings which are generally agreed upon at present. For instance, thin coats of the type of paint used for atmospheric protection are unsatisfactory for underground pipe coatings. They do not have sufficient mechanical resistance to withstand the treatment to which the pipes are subjected before, during and after installation. Although rust inhibiting pigments in such paint coatings offer a measure of defense at the metal surface, they cannot be relied upon without appreciable further reinforcement to withstand the impact stresses during back filling and the subsequent soil stresses. In this connection it would be of interest to experiment with modern baked synthetic types of coating, inasmuch as these offer an attractive combination of moisture impermeability, inhibitive protection in the priming coat, and a high level of mechanical resistance. A minimum 2-coat, or preferably a 3-coat application at the mill in suitable conveyorized mechanisms should make the cost of such protection competitive with other means of protection.

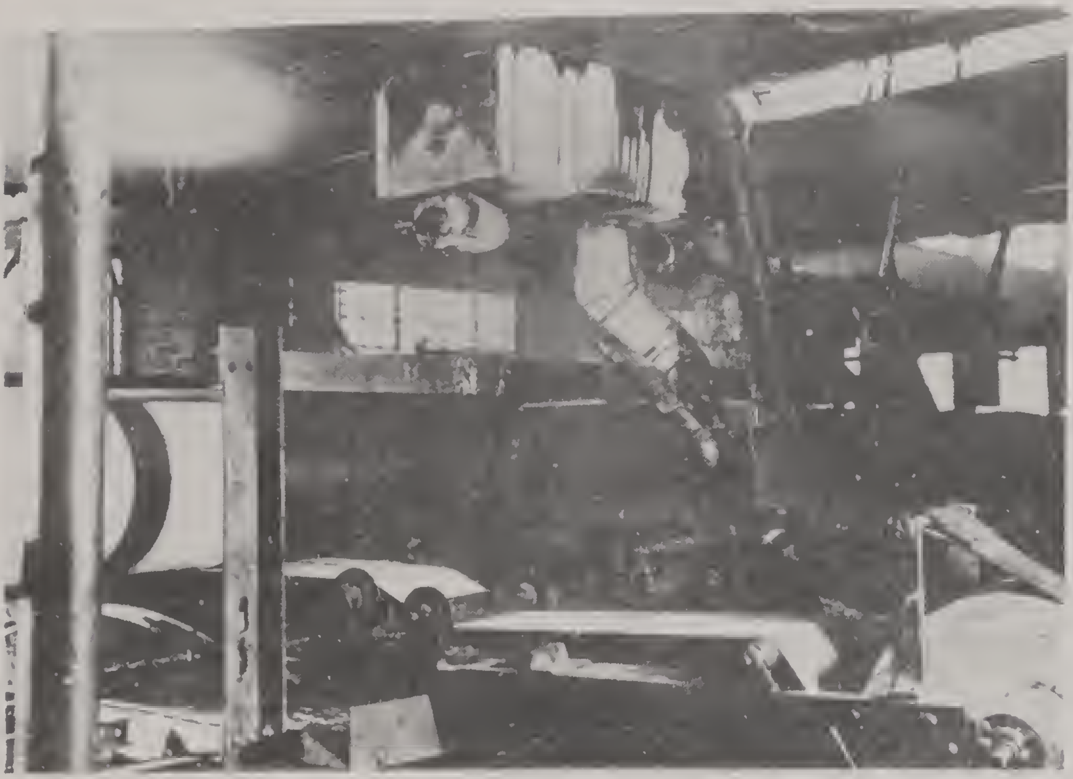
It is generally agreed that thick coatings are desirable. These usually involve a multiple application of the coating medium which automatically minimizes the probability of continuous imperfections through the protective material. Also it helps to decrease the permeability and to delay the effects of soil stresses. These soil stresses are of several kinds. There is the immediate impact of stones and agglomerations during the back-fill operation. Then there is the gradual and variable settling of the back-fill soon after burial of the pipe, and finally there is the swelling and shrinking of the soil as it picks up and loses water. This latter is particularly noticeable in finely dispersed colloidal types of clays in which the swelling pressures at times become quite large.

Owing to these soil stresses, it has been found that reinforcing or shielding of the organic coatings is necessary in most soils. Many methods of improving the mechanical resistance of coatings, particularly those of a bituminous nature, have been tried. Usually the coal tar or asphalt enamels, which are at present the most widely used pipe coating materials, are compounded with the proper quantity of finely dispersed mineral fillers in order to enhance the mechanical resistance of the bituminous coating. Another method of protecting the organic coating against soil stresses consists of the use of strong wrappings between layers and on top of the coatings. A large number of materials have been tried for this purpose, such as cloths of various types, *e.g.*, Hessian, Osnaburg, burlap, etc., metallic foils, cellulosic foils, and impregnated asbestos fabrics or sheetings. Many of the organic fabrics have been found to rot in a number of soils owing to bacterial attack. However, thorough impregnation with a coating medium to a large extent overcomes this defect. In the opinion of many, the asbestos type of shield has given the best performance record, being both mechanically tough and durable.

Of the bituminous coatings, air-blown asphalts obtained from asphaltic crude oils and the coal tars are enjoying the widest use. Although there is some difference of opinion as to the relative merits of these two materials, both of them give good service if properly applied in sufficient thickness. They are by-products of the oil and coke industries, respectively, and hence the care used in their chemical control is not as great as that exercised in the manufacture of paints. Instead, these materials are usually processed to meet specified physical requirements, such as penetration tests, ring and ball softening points, and other empirical deformation tests. As a rule, the coal tars show a narrow range of temperature, beyond the limits of which they become too soft to stay in place or too brittle to resist impact. The addition of fillers and suitable plasticizers has extended this temperature range. The air-blown asphalts, as a class, show a greater temperature insensitivity, but on the other hand are more permeable to moisture than coal-tar coatings. In addition to the bituminous coatings, other materials are also used for specific purposes. Among these are the concrete coatings (See Chapter 16, page 385), grease coatings containing inhibiting chromates, and rubber coatings.

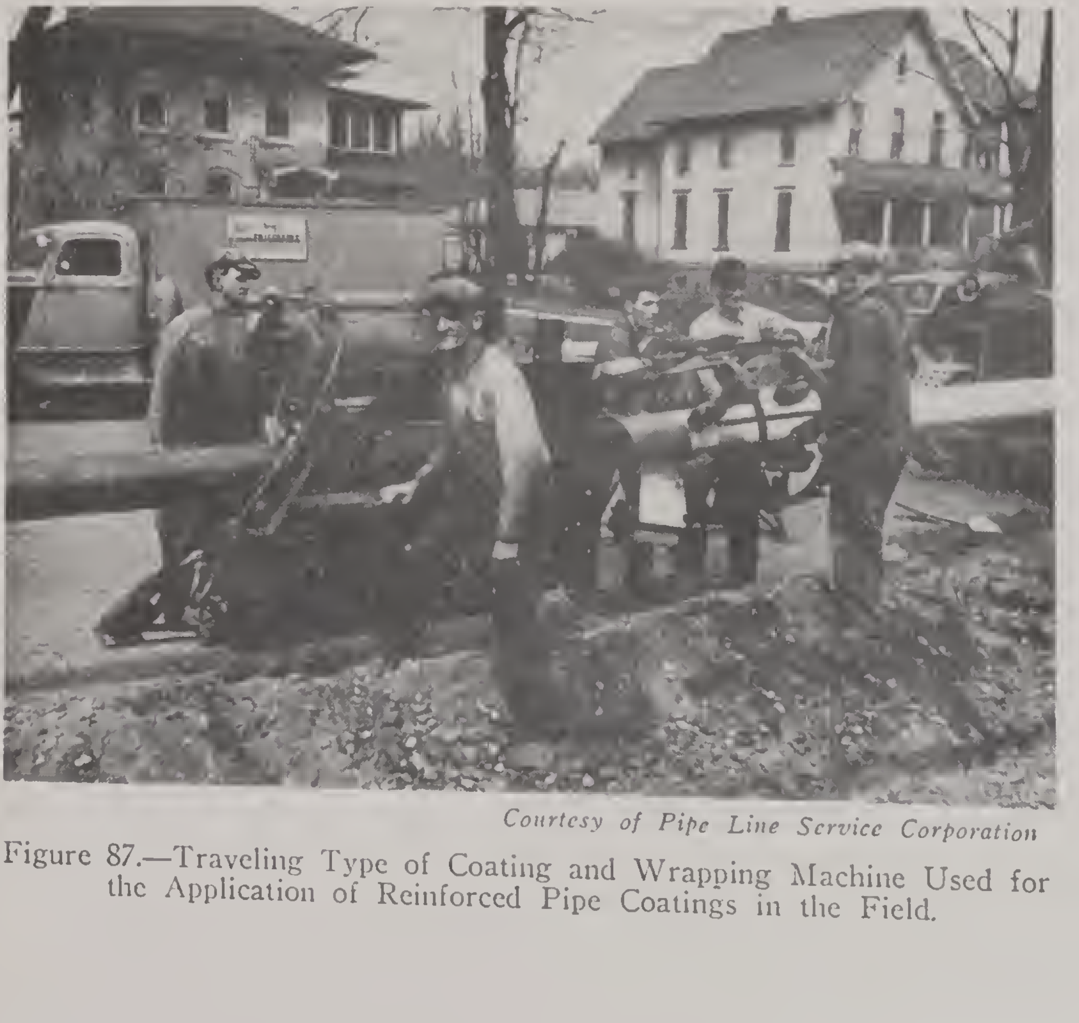
Perhaps the most significant development in the pipe coating field during the past few years has been the improvement in methods of applying the protective coatings. It has been recognized that the proper aim in these developments is toward the perfect coating, that is, one which is completely free of pinholes or "holidays," *i.e.*, missed spots; is adherent to every part of the pipe surface; and is capable of excluding moisture and resisting soil stresses. To make such a coating possible, close control and means of testing of every step in the coating process is necessary. The art has at present developed to a point where one company has considered it safe practice to reduce the wall thickness of its steel pipe and thereby actually effect a net saving even though an improved coating is applied.

Two general methods of applying protective coatings to pipe are now being practiced. One consists of applying the coatings at the pipe factory (Figure 86) and shipping the coated pipe to the point of installation, and the other consists in applying the coatings in the field (Figure 87). In either case the control of process operations has been brought to a high order. The materials used for the coatings are carefully selected. Laboratory tests are made on test panels of eligible materials for such properties as sagging at moderately high temperatures, embrittlement at low tempera-



Courtesy of Hill, Hubbell and Company, Division of General Paint Corporation

Figure 86.—Factory Application of Reinforced Bitumen Pipe Coating.



Courtesy of Pipe Line Service Corporation

Figure 87.—Traveling Type of Coating and Wrapping Machine Used for the Application of Reinforced Pipe Coatings in the Field.

tures, cold flow over long periods, permeability to moisture, and behavior during heating, that is, changes in viscosity and composition. In addition, control tests are used to make sure that subsequent shipments of an accepted coating material are up to standard. Such identification tests as melting point determinations, needle penetrations, and viscosity tests serve for this purpose. During application the heating of the bituminous enamels is carefully regulated inasmuch as temperatures which are too low prevent adequate flow of the coating material and temperatures which are too high, particularly if maintained, bring about thin coatings as well as excessive and harmful decomposition. It is customary to specify a maximum time at top temperatures, beyond which the material must be discarded.

Following is a typical modern factory-applied pipe coating of good quality: The bare pipe is carefully cleaned, moisture, grease, dirt, etc., being removed. The pipe is then fed into a priming machine, where a thin coat of unfilled bitumen, either of asphaltic or coal-tar nature, is applied cold in solution form. This is necessary to obtain adhesion of the hot enamel coat, which otherwise would chill against the cold pipe without thoroughly bonding to it. After the primer has dried, a thick hot coating of enamel, again either of blown-asphalt or coal tar, is flowed over the rotating and forward-moving pipe, which is then immediately served with a spiral and partially over-lapping wrap for mechanical protection of the enamel. Impregnated asbestos felt has been found to be an excellent material for this purpose. A second hot coating of enamel, again followed by a wrap with asbestos felt, is usually applied for high-grade coatings. The final wrapping usually consists of kraft paper, applied immediately after the felt wrapping. This serves to maintain the coating at a lower temperature on direct exposure to the sun and to reveal damage to the coating in the course of shipment. One of the features of the development of these new pipe coatings is the special mechanical equipment needed for the rapid method of application. There is some variation in different commercial coatings both in the materials used and in the number of coats applied. The coating is finally tested for continuity and thickness. Continuity is usually determined by subjecting the entire surface area of the coating to a spark test at a voltage ranging from 5000 to 30,000 volts and the thickness is tested by the weight of the coating on definite lengths of the pipe. Depending on the number of coats applied and the pipe size their thickness ranges from $\frac{1}{32}$ to approximately $\frac{1}{2}$ inch.

Larger pipe sizes are frequently coated in the field with the use of similar machinery. For reconditioning used pipe in the field special machines employing rotating knives, scrapers, and brushes have been developed to remove rust, scale, and incrustations. Pits are filled by welding and the cleaned surface is coated by processes similar to those described for factory applied coatings. One large company has developed a coating composition consisting of a mastic of asphalt and small gravel, properly proportioned to produce a thick rock-like coating of high strength. This coating is directly extruded on the pipe as it passes under a hopper. With some of these field applications as much as two miles of pipe can be coated in one day with an experienced crew. Within the past few years it has become fully realized that care must be exercised in the manipulation and laying of coated pipe. Padded skids and slings are being used and the back-fill is deposited as gently as possible. Although life data on these newer coatings and practices are not as yet available the expectation is that considerably improved performances over coatings applied according to previous methods will be obtained.

Chapter 16

Miscellaneous Coatings

There is a growing number of protective coatings finding commercial use which are neither of the metallic nor the paint type. Some of these, for example, ceramic and chemical-dip coatings, have been employed for years, while others, notably oxide coatings on aluminum, are of more recent development. In any case, considerable progress has been made in the quality of protection to be obtained from these coatings, and some of the processes have assumed outstanding importance.

Electrolytic Oxide Coatings on Aluminum

The anodic oxidation of aluminum and its alloys produces a surface coating which is totally unlike the metal in character, and possesses a rather remarkable group of properties. When properly prepared, this "anodized" coating displays relatively high resistance to corrosion and abrasion and provides high electrical insulation to the underlying metal. It may be colored[1] with a variety of organic dyes and pigments to produce attractive decorative effects. Because of these qualities, oxidized aluminum coatings are coming into common use for the protection and decoration of a wide variety of aluminum products.

The tendency of aluminum to form a superficial film when made the anode of an electrolytic cell has been known for many years. The unidirectional current characteristics of this film, or electrolytic valve action as it was called by Wheatstone in 1855, became the subject of considerable investigation, the outgrowth of which has been the aluminum electrolytic condenser and rectifier. Among the early suggested applications of the oxide coating, other than for such electrolytic devices, was its use in the electrical insulation of aluminum wire,[2] and its application to cooking utensils to prevent adherence of food.[3] It was not until 1924 that the first process of producing relatively thick anodic coatings on aluminum for corrosion protection was patented.[4] This process, known as the Bengough and Stuart chromic acid process,[5] was developed for the protection of Duralumin seaplane parts from corrosion by sea-water.[6] It is still extensively used in England and in this country as a finish, and as a surface pretreatment before painting, for aircraft parts fabricated from aluminum and its alloys.[7] The chromic acid process has been largely superseded in the United States and Europe for most other uses by a process employing sulfuric acid solutions [8] as electrolyte, and in Germany and Japan oxalic acid [9] is said to be used.

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[1] Flick, F. B., U. S. Patent 1,526,127 (Feb. 10, 1925).

[2] Chubb, L. W., U. S. Patents 1,068,410 and 1,068,411 (July 29, 1913); Presser, U. S. Patent 1,117,240 (Nov. 17, 1914).

[3] Mershon, U. S. Patent 1,065,704 (June 24, 1913).

[4] Bengough, G. D., and Stuart, J. M., British Patent 223,994 (Nov. 3, 1924); and later U. S. Patent 1,771,910 (July 29, 1930).

[5] Exclusive rights for the use of this process in the United States are held by the Aluminum Company of America.

[6] Bengough, G. D., and Sutton, H., *Engineering*, 122, 274 (1926); Bengough, G. D., and Stuart, J. M., "The Anodic Oxidation of Aluminum and its Alloys as a Protection Against Corrosion," *Report of Dept. Sci. Ind. Research, H. M. Stationary Office*, 1926.

Common to all methods of anodizing is the necessity of securing an initially clean metal surface. This is usually accomplished by a brief immersion in a warm alkali cleaner suitably inhibited if necessary to prevent attack on the metal. The parts are sometimes dipped in strong alkali to produce an etched or diffusing surface; this treatment is followed by a dip in nitric acid. Traces of the cleaning solutions are removed by thorough rinsing in water before subjection to the anodic treatment.

In the chromic acid process, mentioned above, a 3-per cent solution of chromic acid is used and maintained at 40-45° C., cooling coils being required because of the liberation of heat in the operation. Upon immersion of the work in the solution, the voltage is raised to 40 volts during 15 minutes, maintained there for some time, and then raised to 50 volts, the total time taken being about 1 hour. The current density employed ranges from 0.27 to 0.43 ampere per sq. dm. (2.5 to 4 amperes per sq. ft.). The coating is finally rinsed and dried.

The "Eloxal" process of oxidation originally consisted in anodically treating aluminum in dilute oxalic acid to which had been added a small percentage of chromic acid. The bath was operated at 15 to 30° C., with an applied voltage of 60 to 100 volts and a current density range of 60 to 300 amperes per sq. dm. Now, however, the procedures of the "Alumilite" process are available in Europe and are used in Germany under the trade-name "Eloxal."

The most important anodizing process is the "Alumilite" process employing sulfuric acid as electrolyte. Among its advantages are lower cost, rapidity, low voltage operation and the production of colorless and transparent films of a greater range of physical properties on aluminum and a wide variety of aluminum alloys. One commercial limitation of the chromic acid process is the necessity of "batch" operation to secure the full voltage treatment. It is restricted also to alloys of aluminum containing not more than approximately 4 to 5 per cent of heavy metals. The sulfuric acid process is not subject to these limitations; almost all of the important aluminum alloys, whether wrought or cast, may be treated, and if desired the oxide films produced on these materials may be colored.

Films having a rather wide range of thickness and hardness may be produced in sulfuric acid solutions by suitable adjustment of acid concentration, temperature and time. The acid strength has been varied from 5 to 77 per cent by weight, and the temperature from about 16 to 40° C. (60 to 105° F.). A standard uncolored coating is produced in 15- to 18-per cent sulfuric acid operated for 30 minutes at 22° C. (71° F.). The temperature must be held constant within 2 or 3 degrees if the best coating is to be produced. The process is operated at about 1.4 amperes per sq. dm. (13 amperes per sq. ft.), and this requires from 10 to 20 volts D. C.

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[7] Johnson, R., *Elec. West*, **70**, 158 (1933); Mandeville, D. C., *Engineer (Metallurgist)*, **11**, 58 (1937).

[8] Gower, C. H., British Patent 290,901 (1928); Bengston, H., U. S. Patent 1,869,041 (July 26, 1932); Tosterud, M., U. S. Patent 1,900,472 (March 7, 1933). These patents are controlled by the Aluminum Company of America.

[9] Kenkyujo, British Patent 226,536 (1925); U. S. Patent 1,735,286 (Nov. 12, 1929); Seton, *et. al.*, 1,735,509 (Nov. 12, 1929).

Considerable variation in the process may be made to suit manufacturing conditions provided this variation is held within certain limits. The current tends to form oxide at the surface of the metal, whereas the acid electrolyte tends to dissolve the oxide so formed. Increasing the acid concentration or the temperature increases the attack on the oxide. While the effect of current density is less pronounced, the use of higher current densities tends to counterbalance the rate of oxide dissolution. Films produced under conditions of higher solubility are softer, more porous, and somewhat more flexible than those obtained at lower temperatures and acid concentrations. By appropriate combinations of temperature and concentration it is possible to produce similar films under different operating conditions. For instance, coatings of similar abrasion resistance may be obtained from 5-per cent acid baths operated at 32° C. (90° F.), and 18-per cent acid at 24° C. (75° F.). However, the coatings formed in the two cases are not identical, the first being somewhat more dense than that formed in the second case.

Following the anodizing operation, the oxide coating is usually "sealed" by immersion in boiling water,[10] or in live steam for a period of time equal to that of the electrolytic treatment. By this step (which must be carefully controlled to obtain a uniform product), the oxide comprising the coating is partially converted into the monohydrate of a somewhat greater volume. The result is a reduction in film-porosity and also in hardness, improving the corrosion resistance and stain resistance, but reducing hardness and resistance to abrasion. This treatment largely prevents the tendency of the oxide to "chalk" upon prolonged exposure to the air.

Where corrosion resistance is the primary consideration, it has been found advantageous to substitute for the hot-water sealing operation a treatment in hot dilute dichromate or sodium silicate solutions at 80° C., or in dilute chromic acid solution.[11] The dichromate seal is particularly effective in improving the corrosion resistance of thin films. Lanolin, paraffin or linseed oil are sometimes used as impregnants to improve the corrosion resistant quality of the coating.

In the production of oxide coatings which are to be colored, it is desirable to employ films which are relatively soft and porous, and these are usually prepared, as previously described, by the use of the higher acid concentrations and temperatures. The colors used may be dyes or mineral

[10] Bengston, H., U. S. Patent 1,946,147 (Feb. 6, 1934).

[11] Edwards, J. D., U. S. Patents 1,946,151, 1,946,152 and 1,946,153 (Feb. 6, 1934).

pigments.[12] Usually, acid colors of the alizarin type are employed; these are applied by immersing the anodized part for a few minutes in a warm solution of the dye. The dyed coating is then sealed in hot water or in a hot dilute solution of nickel acetate, the latter improving the fastness of the dye. Mineral pigments are applied by precipitation within the pores of the coating. For example, a yellow may be produced by first treating the anodized coating with a solution of potassium dichromate, rinsing and then treating with a solution of lead acetate.

The thickness of electrolytic oxide coatings in commercial use ranges from approximately 0.0001 to 0.001 inch. For protection against corrosion a film-thickness of the order of 0.0004 inch generally gives good results. As previously mentioned, sealing with hot water or an alkali dichromate are measures designed to improve its protective value. If not physically injured, properly prepared oxide coatings should protect aluminum and its alloys for several years against corrosion by ordinary outdoor atmospheres. Indoors, the life of such coatings appears to be almost indefinitely long. In severe marine exposures it is customary to secure additional corrosion resistance by application to the anodized surface of paints of the aluminum-pigmented synthetic-resin type.

The hardness of the electrolytic oxide film on aluminum varies somewhat with the distance from its outer surface, the hardest region being next to the metal-oxide interface. In Table 44[13] is given the relative hardness (as determined by the Bierbaum test) of the hard and soft oxide finishes in comparison with the hardness of some other materials.

Table 44.—Relative Hardness of Oxide Films on Aluminum.

		Oxide Film on Aluminum	Hard Finish	Soft Finish
Aluminum	80			
Razor steel	1550	Face of film	140	180
Glass	2000	Center of film	3000	1200
Chromium	3100	Base of film	5000	1550

The abrasion resistance of oxide coatings (determined by the abrasive air-blast method described in Chapter 14) has been measured on the same series of coatings by two laboratories with fairly close agreement. The results of these measurements are given in Table 45.[14] It will be observed that abrasion resistance increases with coating thickness.

As mentioned earlier, the anodized finish displays high electrical insulation. It is reported[13] that values of dielectric strength up to 4000 volts are obtainable with the hardest films. In films of commercial importance, it is usual to secure values of breakdown voltage in excess of 200 volts. Probably the most convenient test of coating quality is its breakdown voltage. The relation of film thickness to breakdown voltage for coatings

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[12] Tosterud, M., U. S. Patent 2,018,388 (Oct. 22, 1935).

[13] Mandeville, D. C., *Engineer (Metallurgist Supplement)*, 11, 58 (1937).

[14] Edwards, J. D., *Proc. Am. Soc. Testing Materials*, **37**, Pt. 1, 261 (1937).

Table 45.—Resistance of Oxide Coatings to Abrasion as Determined by the Abrasive Air-Blast Method.

Tests by Bell Telephone Laboratories

Sample	Grams of "Carborundum" Required to Wear Through Coat [a]				Ratio of Abrasion Resistance to Thickness in mils × 10^2
No. A-1	23	24	26	25	
No. A-2	27	30	26	28	
No. A-3	31	28	30	28	
Average		27.1			1.78
No. B-1	66	65	66	68	
No. B-2	68	69	72	70	
No. B-3	73	75	74	73	
Average		69.9			2.33
No. C-1	94	98	97	99	
No. C-2	97	102	97	100	
No. C-3	106	105	104	103	
Average		100.2			2.28
No. D-1	123	125	129	126	
No. D-2	126	129	130	126	
No. D-3	133	136	137	139	
Average		129.9			2.18
No. E-1	44	42	45	45	
No. E-2	40	39	40	41	
No. E-3	41	39	40	41	
Average		41.4			2.41
No. F-1	76	77	80	80	
No. F-2	80	84	89	86	
No. F-3	86	87	92	85	
Average		83.5			2.58
No. G-1	103	102	109	104	
No. G-2	111	111	114	114	
No. G-3	115	116	114	113	
Average		110.5			2.42
No. H-1	143	143	147	148	
No. H-2	154	153	155	165	
No. H-3	158	161	157	160	
Average		153.7			2.54

Tests by Aluminum Company of America

Sample	Grams of "Alundum" Required to Wear Through Coat [b]				Ratio of Abrasion Resistance to Thickness in mils × 10^2
No. A-6	28	35	32	28	
	30	28	28	30	
Average		29.9			1.97
No. B-6	71	74	71	73	
	72	72	71	73	
Average		72.1			2.40
No. C-6	115	111	106	110	
	110	111	108	110	
Average		110.2			2.50
No. D-6	149	150	148	147	
	147	146	148	148	
Average		147.9			2.48
No. E-6	36	35	36	35	
	35	34	34	35	
Average		35.0			2.03
No. F-6	77	80	80	76	
	80	79	81	78	
Average		78.9			2.44
No. G-6	125	123	116	116	
	119	120	120	119	
Average		119.8			2.63
No. H-6	161	163	160	160	
	165	160	162	160	
Average		161.4			2.67

[a] The method, as operated by the Bell Telephone Laboratories, employs 180-mesh "Carborundum" in an air blast under a pressure of 10 cm. of mercury. The specimen is set in contact with the end of the air-blast nozzle at an angle of 45 deg. through the vertical nozzle. The first two abrasion values in each horizontal column were measured on the front of the specimen, the second two values on the reverse side.

[b] The method, as operated by the Aluminum Company of America, employs 180-mesh "Alundum" in an air blast under a pressure of 5.17 cm. of mercury (approximately 1 lb. per sq. in.). The nozzle is set ¾ in. from the surface of the specimen and with the specimen at an angle of 45 deg. to the vertical nozzle. The four values in the first horizontal column for each specimen were measured on the front face of the specimen, the second column of four on the reverse side.

produced by one of the standard sulfuric acid processes is given in Figure 88.[13]

The applications of anodized coatings have become extensive. Their oldest and perhaps most general application is in aircraft. The combination of electrical insulation and corrosion resistance has made it particularly useful in electrical apparatus. They are commonly employed to increase the corrosion resistance of aluminum and aluminum alloy articles, such as refrigerator ice-trays and apparatus parts. Because of the hardness of these coatings, the finish is used on machine parts and pistons to protect against abrasion, seizure and to reduce friction. The colored finish is used on small articles, furniture and fixtures of various kinds. In the architectural field, oxide coatings are employed extensively for window frames, store fronts and interior fittings. The Empire State Building in New York City carries over 5000 aluminum alloy spandrels covered with a gray oxide coating.[15] The transatlantic liners *Queen Mary* and *Normandie* and the new streamlined trains use anodized coatings both for decoration and corrosion prevention.

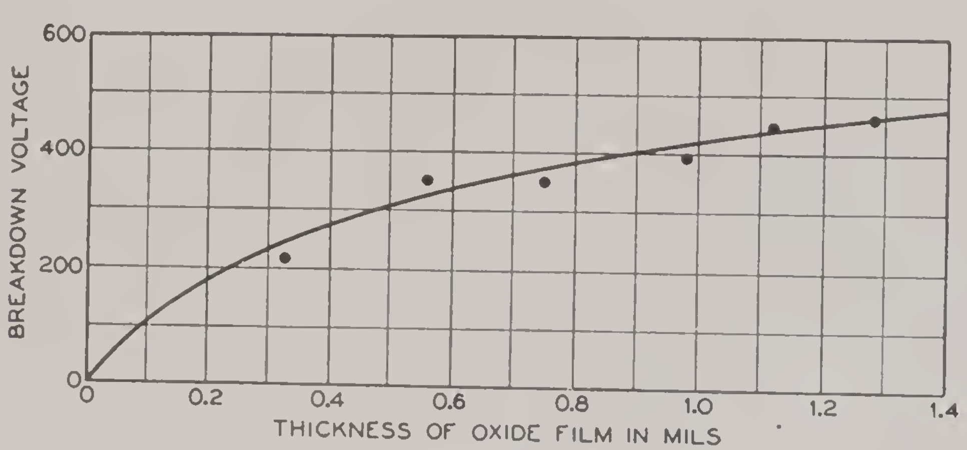

Figure 88.—Breakdown Voltage of Oxide Films on Commercially Pure Aluminum.

Surface Conversion or Chemical-Dip Coatings

Protective coatings produced by converting the surface of a metal into an oxide, salt or other chemical compound of exceedingly low solubility in the environment to which it is to be exposed are becoming of great importance. As has been repeatedly mentioned in foregoing chapters, the resistance of most metals to corrosion is due to the formation on their surfaces of relatively insoluble corrosion products by reaction with non-metallic elements of their surroundings. By the choice of proper solutions and conditions it is possible to produce coatings of this type on almost any metal. Naturally the principal industrial interest is in suitable coatings for steel, and for this purpose it has been found that surface films formed in phosphate and chromate solutions have been the most satisfactory. These coatings have been found to be particularly suitable as a basis for the application of paint and enamel coatings and are now almost universally used in the automobile industry for that purpose.

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[15] Edwards, J. D., *Product Eng.* (March, 1931).

There is evidence that the use of phosphates for the protection of certain iron articles was known to the Romans in the third century A. D.[16] In 1869 it was observed [17] that rusting of the metallic parts of women's corsets was retarded by treating them with phosphoric acid. The first important commercial application of phosphate coatings followed the proposal of Coslett in 1908 to treat iron and steel parts in a solution of phosphoric acid and ferrous sulfate in definite proportions.[18] Later Coslett substituted zinc sulfate for the ferrous sulfate, and in 1918 it was found by the Parker Company [19] that the character of the coating was improved by the use of a solution of primary manganous phosphate. In this process, which came to be known as "Parkerizing," manganese dioxide was added to the bath, it being claimed that oxidation of at least some of the phosphate to the form of ferric phosphate was essential. The time required for treatment was usually from 3 to 4 hours. While the Coslett process known as "Coslettizing" was rather widely used in England for phosphating the steel parts of bicycles and other articles, neither it nor the original Parkerizing process were suited to the needs of the rapidly expanding finishing industry.

The Parker process was improved in 1926 by the adoption of manganese di-hydrogen phosphate for the processing solution. This made possible a reduction in time of treatment. Somewhat later a further reduction in processing time to about 10 minutes was effected by incorporating a small percentage of a copper salt in the bath. This permitted the use of the process in a conveyorized or line finishing system.[20] The increasing use of phosphate coatings as a base for paint was reflected in the name, "Bonderizing," given to the improved process.[21] Still later improvements have been in the direction of time reduction and spray application. The processing time is now from 30 to 60 seconds, employing the solution at 180° F. in the spray application. Solutions of zinc phosphate containing alkali nitrates [21a] or nitrites [21b] may be used.

In Figure 89 is shown a cut-away photograph of the equipment used in this process. Instead of the spraying step, dipping may be used for certain classes of work. Following treatment in the phosphate solution and a cold-water rinse, it is customary to treat in a dilute chromic acid or sodium dichromate solution at 200° F., and after this to dry without

[16] Jacobi, L., "Das Römerkastel Saalsburg bei Homburg vor der Höhe," pp. 158, 201, 203, Homburg, 1897; Macchia, O., *Ind. Meccanica*, 17, 617 (1935).

[17] Tanner, R., *Monthly Rev. Am. Electroplaters' Soc.*, 21, (Dec., 1934).

[18] Thornton-Murray, M., *Engineering*, 85, 870 (1908); Blassett, E., *Metal Ind. (N. Y.)*, 9, 207 (1911).

[19] *Chem. Met. Eng.*, 18, 214 (1918); Eckelmann, L. E., *Chem. Met. Eng.*, 21, 787 (1919); *Raw Materials*, 5, 438 (1922).

[20] U. S. Patent 1,888,189.

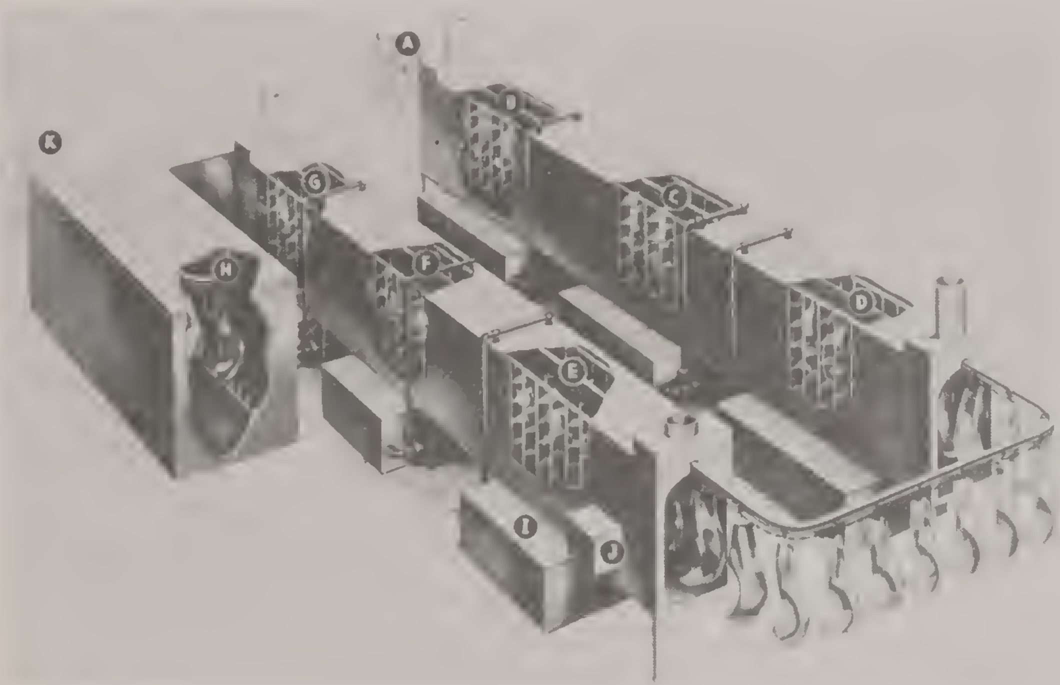
[21] Darsey, V. M., *Ind. Eng. Chem.*, 27, 1142 (1935).

[21a] Tanner and Lodeesen, U. S. Patent 1,911,726 (1933).

[21b] Parker Rust-Proof Co. vs. Borg-Warner Corp., U. S. Patent Quart., 38, 468 (1938).

rinsing and to paint. Before the general use of paints on Parkerized coatings it was the practice to apply oils, waxes, etc., and for certain purposes phosphate coatings of this type are still used. It seems hardly necessary to state that metal parts must be thoroughly cleaned before application of phosphate coatings.

A good deal of the success of this coating as a base for paint coatings has been due to the production of a surface-film which is uniform, fine-grained and strongly adherent to the basis metal. From chemical analyses it appears that the film is composed chiefly of a mixture of iron and phosphate compounds. There can be no doubt too that the phosphate coating does impart an important measure of rust resistance. In addition to steel and cast iron it is possible to Parkerize zinc coatings and zinc-base die-castings. Phosphate coatings on zinc die-castings have been found to improve corrosion resistance several-fold when followed by two coats of a baked synthetic resin enamel.



Courtesy of Parker Rust-Proof Company

Figure 89.—Complete Spray-Phosphating Process from Cleaning to Drying.

A—Production entering cleaning section.
B—Alkaline cleaning.
C—Rinse.
D—Rinse.
E—Spray-phosphating section.
F—Clear-water rinse.
G—Acidified rinse.
H—Drying oven.
I—Tank for spraying-phosphating.
J—Tank for replenishing spray-phosphating solution.
K—Phosphated production leaving the drying oven, ready for final finish.

There are a number of other commercial processes for the production of surface-conversion coatings. These are known by a number of trade-names and consist usually in treatment with phosphate, chromic acid, dichromate or strong alkali solutions.[22] In some cases an alternating current is employed in the process. The corrosion resistance of zinc, zinc coatings and zinc-base die-castings may be increased by treatment in sodium dichromate solutions acidified with dilute sulfuric acid.[23] This treatment is known as the "Cronak" process.

Magnesium and magnesium alloys containing 85 to 99 per cent magnesium when used in ordinary atmospheres, require surface conversion treatments followed by painting. Before the surface treatment, the metal is cleaned by almost any of the usual methods described in Chapter 2. The most widely used chemical treatment for magnesium alloys consists of a simple dip for 30 seconds to 2 minutes in a solution containing 1.5 pounds of sodium dichromate and 1.5 pints of concentrated nitric acid with water to make 1.0 gallon.[24] In other treatments either sodium phosphate, ammonium sulfate or potassium chrome alum is used with sodium dichromate. For naval aircraft use, magnesium alloys may be given a 30-minute anodic treatment in a sodium dichromate-sodium phosphate bath. The priming paint coat applied to the chemically treated alloy usually contains zinc chromate, red iron oxide, or a mixture of the two, and this may be followed by top coats of spar varnish or a synthetic resin enamel.

Aluminum and its alloys may be improved in corrosion resistance by treatment with solutions of oxidizing character such as potassium dichromate A solution which has been recommended for this purpose contains 20 grams of sodium carbonate and 5 grams of potassium dichromate per liter of water.[25] Aluminum boiled in this solution acquires an attractive, smooth gray coating in from 5 to 10 minutes. In another process [26] aluminum is immersed in hot ammoniacal solutions containing small percentages of salts of metals such as silver, nickel, cobalt, etc. These coatings are all of the general type of the phosphate coatings produced on steel and magnesium, described previously.

Protective Films Induced by the Presence of Alkalies and Oxidants

A metal surface may be rendered passive by the presence of substances in the environment which react with the metal to form compounds of low solubility. This process is analogous to that involved in the formation of protective films by the chemical dip treatments described in the foregoing section. It is similar in principle to the film formation which occurs when certain corrosion-resistant alloys are exposed to ordinary environments; in the first case the passivating agent is introduced into the environment. while in the second case it is incorporated in the alloy. One advantage in either case over the chemical dip method of producing protective films lies in the tendency of the films to repair themselves.

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[22] Anon.. *Iron Age,* 136, 34. 76 (Oct. 31. 1935).

[23] Anon.. *Metal Cleaning and Finishing,* 8, 476 (1936): *Steel.* 98, 43 (June. 1936).

[24] "The Surface Treatment and Painting of Dowmetal." The Dow Chemical Co.. Midland. Mich.. March 1. 1938.

[25] Edwards, J. D.. Frary. F. C.. and Jeffries. Z.. "Aluminum Industry," Vol. 2, p. 471, New York. McGraw-Hill Book Co., 1930.

[26] Pacz, A., U. S. Patent 1,551,613 (Sept. 1, 1925).

There are many instances where it is feasible to protect metals by the introduction of alkalies or strong oxidants. For example, the use of sodium dichromate crystals in automobile radiators (two-thirds of an ounce to a gallon of water) will prevent rusting. All sorts of tanks or circulating systems using water or brines may be protected by such means. It must be pointed out, however, that the nature of the water or solution, that is, the presence of chlorides and sulfates, in particular, will have a bearing on the concentration of protective agent which will be required. Insufficient quantities of the retarder are likely to accelerate localized corrosion.[27] In addition to iron and steel, which are readily protected by soluble chromates, other metals, such as aluminum, copper, brass, lead, zinc and zinc-coated iron, may be passivated by the same means in water and in salt solutions under certain conditions.

An important application of film-protection by the use of alkalies and oxidants is in the field of air-conditioning where the equipment is exposed to recirculated water, water spray and humid atmospheres. The water after a few hours of operation becomes highly contaminated by substances absorbed from the atmosphere and is usually saturated with air. This is shown in Table 46 [28] in which is given the composition of the water, before and after use, in three cities and two types of industrial plants. Included also in this table are the results obtained in corrosion tests on small specimens of copper-bearing steel inserted for a period of ten days in air-conditioning equipment in operation. One set of four specimens was completely immersed in the tank water and another similar set in the spray between opposing banks of spray.

From these results it will be seen that a mixture of sodium dichromate, containing either sodium hydroxide, carbonate or silicate, gave the most satisfactory performance. Both bare and galvanized copper-bearing steel are used in the construction of air-conditioning equipment and readily accessible surfaces are usually painted with bituminous paints. There remains, however, a considerable area to which protective paints cannot be applied and it becomes necessary to devise methods, such as that described above, to control corrosion. Tests have indicated that the amount of chromates carried over into the conditioned space is very small.[28]

PRESERVATION OF METALS AND MACHINERY BY SLUSHING COMPOUNDS

Machine parts of all kinds, guns, rifles, and various articles of hardware which are placed in storage, or stand idle for indefinite periods of time, require protection against corrosion. It is essential that the protective agent should remain in place, prevent corrosion, that it should be unreactive toward the metal, resistant to oxidation, and that it should be easy to

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[27] Roetheli, B. E., and Cox, G. L., *Ind. Eng. Chem.*, 23, 1084 (1931).

[28] Sterne, C. M., *Proc. Am. Soc. Testing Materials*, 35, Pt. 2, 261 (1935).

Table 46.—Weight Losses in Milligrams per Square Inch, Average in Each Class of Test.

Duration of tests 10 days. Average of 4 test specimens in each case.
Analyses of raw water and water at end of one week's run shown at each location.

	New York City 7 Days Use		Philadelphia 6 Days Use		Washington, D. C. 6 Days Use		Tobacco Plant[d] 7 Days Use		Rayon Plant 7 Days Use	
	Raw Water	Continuous	Raw Water	10 hr. (Day)	Raw Water	8 hr. (Day)	Raw Water	Continuous	Raw Water	Continuous
Silica, p.p.m. ...	2.1	2.5	4.8	5.1	7.4	4.5	13.0	27.0	3.6	18.0
Iron oxide, p.p.m.	0.4	475.3	5.1	86.8	1.8	26.2	1.8	63.6	1.1	374.0
Calcium oxide, p.p.m.	8.8	37.0	25.4	32.5	49.4	46.2	17	31.0	33.0	176.0
Magnesium oxide, p.p.m.	2.1	6.4	11.7	13.7	12.5	15.6	1.6	7.4	4.0	26.0
Bicarbonates, p.p.m.	7.5	...	32.5	12.1	42.6	48.4	60.0	...	20.0	...
Carbonates, p.p.m.	...	...	...	...	37.8	...	...	...	...	...
Chlorides, p.p.m.	3.3	19.5	16.2	48.2	9.2	33.6	3.5	15.3	10.0	42.0
Sulfates, p.p.m..	6.1	476.2	24.8	116.3	11.2	54.7	21.0	82.0	25.0	670.0
pH value	7.0	3.3	7.1	4.9	7.5	6.1	7.2	4.7	8.1	3.0
Treatment	Total Immersion	Sprays	Total Immersion	Sprays	Total Immersion	Sprays	Total Immersion	Sprays	Total Immersion	Sprays
None[a]	115.4	268.2	85.3	188.7	66.0	146.0	158.1	302.6	197.7	396.1
No. 1	0.4	0.5	0.4	0.4	0.4	0.4	0.5	0.6	0.8	0.9
No. 2	2.0	1.1	1.5	1.0	1.5	1.1	[c]	[c]	2.6	3.0
No. 3	8.2	7.5	7.4	7.0	[c]	[c]	16.4	22.1	18.3	25.6
No. 4[b].........	54.6	70.1	46.1	59.3	[c]	[c]	59.2	78.6	63.5	82.3
No. 5[b].........	53.0	69.2	46.0	58.7	[c]	[c]	57.6	74.3	62.1	80.9
No. 6	37.4	32.4	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]
No. 7	33.1	28.6	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]
No. 8	16.1	17.3	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]
No. 9	3.0	2.1	3.1	2.4	[c]	[c]	[c]	[c]	[c]	[c]
No. 10[a]........	110.6	255.0	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]
No. 11[a]........	113.0	256.3	82.9	182.3	[c]	[c]	[c]	[c]	[c]	[c]
No. 12[b]........	52.6	67.1	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]
No. 13[b]........	51.7	65.2	46.2	59.1	[c]	[c]	[c]	[c]	[c]	[c]
No. 14[b]........	45.2	59.3	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]

[a] General heavy corrosion on test pieces.

[b] Total immersion test specimens in all tests in all locations using treatments Nos. 4, 5, 12, 13, 14 badly pitted.

[c] No test run.

[d] 6 p.p.m. chlorine for algae and fungi control, with periodic dosages of 5 p.p.m. copper sulfate used in tobacco plant air-conditioning equipment.

NOTE.—The treatments referred to were as follows:

Treatment	Concentration of Main Constituents in Recirculated Water	Average pH Value in Recirculated Water During Test	Solution Used
No. 1.....	500 p.p.m. sodium dichromate......	7.5-8.0	(1) 42% sodium dichromate, 6% sodium hydroxide. (2) 40% sodium hydroxide, 9% sodium dichromate.
No. 2.....	350 p.p.m. sodium silicate as SiO_2.. 120 p.p.m. sodium dichromate......	8.0-8.5	28.3% sodium silicate, 4.5% sodium hydroxide, 3.2% sodium carbonate, 9.1% sodium dichromate, 1% trisodium phosphate.
No. 3.....	50 p.p.m. sodium dichromate......	8.0-9.0	40% sodium hydroxide, 9% sodium dichromate.
No. 4.....	....	8.0-9.0	48.3% sodium hydroxide.
No. 5.....	....	8.0-9.0	20% sodium carbonate.
No. 6.....	40 p.p.m. sodium silicate as SiO_2..	8.5-9.0	58° Baumé sodium silicate.
No. 7.....	55 p.p.m. sodium silicate as SiO_2..	8.5-9.0	52° Baumé sodium silicate.
No. 8.....	100 p.p.m. sodium silicate as SiO_2..	7.5-8.0	27.4% sodium silicate, trace tannin.
No. 9.....	500 p.p.m. sodium silicate as SiO_2..	8.5-9.0	40° Baumé sodium silicate.
No. 10....	....	7.0-3.9	Tannin, and other undetermined organic material—solution added at rate of 1 qt. to 35,000 gal. of water.
No. 11....	....	7.0-3.8	Tannin, iron, undetermined organic matter—solution added at the rate of 1 qt. to 35,000 gal. of water.
No. 12....	....	8.0-9.0	Treatment No. 11 and sufficient 50° Baumé sodium hydroxide to maintain average pH value.
No. 13....	....	8.0-9.0	Treatment No. 11 and sufficient sodium carbonate to maintain average pH.
No. 14....	300 p.p.m. sodium phosphate as PO_4	7.5-8.5	Tri-sodium phosphate.

apply and be readily removable without injury to the metal surface. This specification would appear to describe a viscous, oily, grease or wax-like substance of the saturated, low-acid, non-drying type. A great variety of substances which meet these requirements to some extent have been used for temporary protection of metal surfaces. These materials are known generally as slushing oils or compounds (and sometimes as "rust preventive compounds"), and may consist of mineral or fatty oils and greases with or without the addition of waxes or soaps. In another type of compound, an inhibitor, such as sodium dichromate, has been used in small amounts in oils or emulsions of oil in water.

One of the first investigations of slushing compounds was undertaken by the Bureau of Standards.[29] From outdoor exposure tests on steel panels coated with various substances of the general nature of slushing oils, it was found that certain grease-like materials of a semi-solid consistency composed of petrolatum mixed with small proportions of wax and rosin were the most effective. These substances compared favorably with the best proprietary rust-preventives of the period.

In a preliminary study of a variety of slushing compounds carried out at the National Physical Laboratory,[30] it was concluded that crude lanolin was the most promising material for the purpose. This conclusion was substantiated in a further and more comprehensive investigation extending over a period of 5 years.[31] It was found that crude lanolin, so processed as to show an acidity not exceeding 2 per cent, calculated as oleic acid, and with a saponification value between 96 and 101 mg. of potassium hydroxide per gram, was suitable for use when dissolved in either white spirit or solvent naphtha. The British Air Ministry specification for temporary rust prevention calls for 35 to 40 per cent by weight of lanolin of the quality given above in equal parts of white spirit and solvent naphtha. The material is applied by dipping or by brushing. A small percentage of a dye is sometimes added by users of the formula. Crude lanolin may be applied to machinery with the hands or by means of a rag, but the coating is likely to be uneven. It may also be applied by spraying, using trichlorethylene as solvent, and in this case, good ventilation must be provided.

The composition of lanolin is not known with certainty.[32] The main constituent, melting in the range 73-75° C. (163-167° F.), is apparently a mixture of esters of cholesterin ($C_{27}H_{45}OH$), a monohydric alcohol, and higher fatty acids of 26 and 27 carbon atoms. Presumably these waxes, consisting of chain-like molecules of more than 50 carbon atoms, provide a unique surface film of high protective quality on the metal surface. It is well known that highly polar molecules of this type are readily adsorbed on surfaces and arrange themselves on end in a closely packed fashion. This molecular behavior may well account for the efficacy of lanolin in the prevention of rusting. It would be expected on this basis that waxes, as a class, should be suitable for use in slushing compounds, although it will be borne in mind that the consistency of the substance and other physical and chemical properties are of importance. A practical advantage in the use of partially refined crude lanolin, as compared with other wax-bearing materials, is its reasonable cost.[31]

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[29] Walker, P. H., and Steele, L. L., *Bur. Standards Tech. Paper No. 176* (Oct. 14, 1920).

[30] Jakeman, C., *Engineering*, 120, 123 (1925).

[31] Jakeman, C., *Dept. Scientific and Ind. Research, Special Report No. 12*, 2nd ed., London, H. M. Stationery Office (1934).

[32] Abraham, E. E. U., and Hilditch, T. P., *J. Soc. Chem. Ind.*, 54, 398T (1935).

Spermaceti wax, or cetyl palmitate, consisting of a chain of 32 carbon atoms, has shown promise in tests [33] as a protective agent for both brass and steel, and it has been used to a limited extent for such purposes. Sperm oil, a liquid wax, has been valued as a substance to prevent rusting of small machine parts. A number of common waxes, such as carnauba and beeswax, have been added to slushing compounds with benefit in some instances, although no advantage was obtained when they were added to lanolin solutions.[31]

Probably the most widely used materials for the temporary protection of machinery have been ordinary commercial mineral oils and petrolatums. A commonly used oil of this type is "mineral seal" oil, a light oil intermediate between kerosene and spindle oil in body. Compounds of this class are not adsorbed by the metal surface, and are likely to be less permanent on account of the ease with which the oil film may be replaced by water. The effectiveness of this type of non-polar compound in protecting metals is almost entirely a direct function of viscosity.[34] Mineral oils have the advantages of stability and low cost and those of high viscosity (particularly petrolatum) provide a fair measure of protection. Heavy fractions which contain, or have added to them, asphaltic substances are more adhesive, and, where low in sulfur and free acid, have shown good protective qualities. Cylinder oils with additions of zinc naphthenate and ceresin have been recommended as slushing oils.[35]

Greases are mixtures or emulsions of soaps and mineral oils employed in lubrication. It is possible to obtain a wide range of characteristics in such substances, and many are used as slushing compounds. Lime soap greases have proved markedly better than soda greases in tests,[33] but as a class, greases are inferior to many other materials as slushing compounds. Mixtures of rosin or rosin oil with mineral oil is another common type slushing compound.[36]

A new type of material which has been proposed [37] for the protection of machinery is obtained from the oxidation of petroleum residues. It consists of a mixture of high molecular-weight ketones, keto-acids and lactones in different proportions. These mixtures are available in a wide range of consistencies varying from that of a light mineral oil to that of a stiff grease. They are of the non-spreading adsorbent type of compound and are employed in lubricating oils for increasing film strength or "oiliness." Laboratory tests [5] have shown these products to have considerable promise as slushing compounds.

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[33] Experiments by Messrs. W. E. Campbell and S. M. Arnold of Bell Telephone Laboratories to be described in a later publication.

[34] Borodulin, M. V., and Nemchinova, V. N., *J. Chem. Ind. (U.S.S.R.)*, 14, 1708 (1937); *Chem. Abst.*, 32, 2331 (1938).

[35] Nemchinova, V. N., *J. Chem. Ind. (U.S.S.R.)*, 15, 48 (1938); *Chem. Abst.*, 32, 3133 (1938).

[36] French Patent 42,769 (Oct. 10, 1933).

[37] Tech. Bull. Technical Service Bureau Inc., Chicago, Ill.

The value of incorporating inhibitors, such as sodium dichromate and zinc oxide in slushing oils, is debatable; recent comparative tests, while not extensive, have not borne out the supposition that additional protection of the metal is obtained by their use.[33] There may be cases where their use can be justified. It has been shown that an alkaline film, remaining on the surfaces of small articles such as steel bolts, screws and hooks after washing them in a soap solution containing a small amount of soda ash, is sufficient to preserve them against rusting during long periods of storage, provided the conditions of storage are reasonably well controlled.[38]

The successful use of slushing compounds depends to a considerable extent upon proper cleaning of the metal surface beforehand, and the application of a uniform film of the compound. It is generally desirable to wipe moisture, grease and dirt from the surface beforehand with a clean rag. The coating may be applied by dipping, brushing, rubbing-on or spraying. Very often the nature of the article to be treated will determine the method of application. Much is to be said in favor of spraying where the fire hazard permits. It is preferable to employ petroleum base solvents for this purpose. In addition to the relatively toxic nature of non-flammable solvents, such as the chlorinated hydrocarbons, carbon tetrachloride,* trichlorethylene, etc., there is definite evidence that coatings applied by means of such solvents are of a lower protective value, possibly because they entrap solvent which subsequently reacts with moisture to produce corrosive substances.

VITREOUS ENAMEL COATINGS

Vitreous or porcelain enamels are essentially fused silicates or glasses holding in suspension a colloidal dispersion of color oxides, opacifiers and gases. They have become of increasing importance as coatings for ferrous materials, and it seems likely that this trend will continue in the future as a result of improvements which are being made in enameling processes and materials. Perhaps the principal field of use for large enameled units has come to be the chemical, pharmaceutical and food industries.[39] Porcelain enamels are available which will resist practically any chemical with the exception of those which will dissolve silicates, such as strong alkalies and hydrofluoric acid.[40] One of the largest distilleries uses porcelain-lined steel processing, storage, and blending units. Similarly, large brewery vats and storage tanks are now coated with enamels of this type. These have been made in single pieces up to 45 feet in length and 12 feet in diameter.[40] One of the most recent developments is that of the glass-lined railroad tank-car used for the transportation of acids, chemicals, and biochemical products. The largest use for truck and car tanks with such linings, however, continues to be in the dairy field. Less than 25 years ago, no enamel was used on stoves, refrigerators, table tops, road signs, or store fronts; these are common applications at the present time. Porcelain enameled steel has been used recently for the exterior of residential buildings.[41] A finish of porcelain enamel adapted to resist soil corrosion of both the acid and alkaline type is in good condition after ten years in soil where the life of steel pipe is 1½ to 2 years. Similarly this type of finish has been used to prevent corrosion on the interior of domestic hot-water storage tanks.[40] Enameled kitchen ware, owing to improvements in quality, has successfully withstood the competition of the growing number of new materials which have been offered in this field.

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[38] Cooper, W. E., *Ind. Eng. Chem.*, 23, 999 (1931).

* See Int. Crit. Tables, II, 319.

[39] Barnes, P. S., *Ind. Eng. Chem.*, 29, 378 (1937).

The art of enameling originated in ancient times and was concerned with the ornamentation of small articles, such as jewelry, cups and small caskets or boxes. The goldsmith and later the coppersmith seem to have worked together with the early glass-blower to develop *Cloisonné* and later *Champleve*. In the former, fine wire partitions were soldered to a gold or copper surface so as to form a border around the designs and then the resulting compartments, or cloisons, were filled with various colored enamels in powder or paste form. It became somewhat simpler to gouge out and carve the ornamental design in the metal base (generally copper) leaving thin fins to prevent the colors from running into each other when fused. This came to be known as Champleve, and both this and Cloisonné reached a high state of development at Byzantium in the early centuries of the Christian era. The enameler's art spread to Western Europe and in the Middle Ages, Limoges achieved a great reputation, particularly for the development of painted enamels—a process in which the designs wre painted either in dark colors on a light enamel, or in light colors on a dark enamel.

The first commercial enameling of cast iron was carried out probably in Bohemia about 1830; it consisted in dusting the enamel in powdered form on the surface of the iron heated to redness and subsequently heating the object to melt the enamel to a smooth glass. A few years later, following improvements in the technology of ferrous materials, sheet-iron and steel were successfully enameled. About this time, new processes for the manufacture of soda and borax provided the enameler with improved raw materials at lower cost. A further marked impetus was given the enameling industry when it was discovered that clay may be used to keep the powdered enamel in suspension in water and cause it to adhere to the metal before firing.[42]

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[40] *Private communication* from Mr. W. W. Higgins, July 27, 1938.

[41] Hansen, J. E. (Ferro-Enamel Corp.), "Manual of Porcelain Enameling," Cleveland, Ohio, Enamelist Pub. Co., 1937.

[42] Andrews, A. I., "Enamels," Champaign, Ill., Twin City Printing Co., 1935. This work, an excellent recent treatise, has been consulted freely in the preparation of the historical material given above.

Among early enameled products, kitchen utensils of the agate or graniteware type were most common. The enameled cast-iron bathtub is said to be a product of Scotland, and the porcelain enameled stove came from Germany.

Much of the improvement in enameling in recent years is the result of coöperation by the steel manufacturer in providing more suitable metal for enameling, and of the designer of equipment who, by taking into account the inherent limitation of enamels, avoids, in his designs, features which are impractical. A good grade of basic open-hearth flange steel free from surface defects, laminations and carbon and slag segregations, and containing not more than 0.13 per cent carbon, 0.04 per cent sulfur, 0.03 per cent phosphorus, 0.05 per cent silicon and from 0.30 to 0.50 per cent manganese, has been found to be most satisfactory for heavy gauges.[43] Where lighter-gauge steel *i.e.,* 14 to 30 gauges, is used, a representative analysis would be 0.3 per cent carbon, 0.25 per cent sulfur, 0.10 per cent phosphorus, a trace of silicon, and 0.05 per cent manganese. Physical characteristics of the lighter-gauge steel are controlled in order to meet the specific conditions for which it will be used, flat panels, deep-drawn objects, etc.[40]

The metal part to be enameled may be annealed to remove strains and burn off oil or grease, or where stress relieving is not necessary, may be cleaned in hot alkali, after which rust and scale are removed by pickling in dilute sulfuric or hydrochloric acid. Sandblasting is employed for heavy-gauge metal.

The raw materials used in vitreous enamels consist of the refractories and fluxes which, upon fusion, produce the glass or "frit;" the floating agents used to suspend the powdered frit in water, yielding thereby what is known as the "slip;" the electrolytes or "set-up salts" which serve to coagulate the slip and give it the proper consistency for application to the metal surface. Metallic oxides are added to the frit or to the slip to produce opacity or color in the enamel. The refractories are acidic substances, such as quartz and feldspar, while the fluxes consist commonly of borax, soda ash, cryolite, fluorspar, sodium nitrate, whiting, litharge, etc., which react basically. As mentioned previously, clay is used as a floating agent, as also is gum tragacanth in special cases.

In the preparation of the enamel by the wet process, the frit, which owes its friability to rapid quenching of the melt in water, is ground in a pebble mill in the presence of water, clay and the opacifier (usually tin, antimony or zirconium oxide) or coloring agent. Red colors are usually made from cadmium, iron, or selenium compounds; green from chromates; yellow from antimony, uranium, or titanium; and blue from cobalt compounds. The mill additions exclusive of water seldom exceed 15 per cent of the frit.

Prior to application, electrolytes such as magnesium carbonate, soda ash or borax may be added to the slip to cause it to "set up" properly. The part to be enameled is either dipped in the slip or, in the case of large surfaces, the slip may be sprayed on the metal. Following this, the enamel coating is dried and then fused or "burned" in an enameling furnace under careful heat control. One to three coats may be applied in this manner, and the first or ground coat always contains cobalt oxide to promote adherence. The manner in which cobalt achieves this end is obscure. It has been suggested that the increased solution of iron in the enamel caused by the presence of cobalt reduces the gradient of the coefficient of thermal expansion between metal and coating; that cobalt silicate is formed with the evolution of oxygen, thereby cleaning the interface between metal and enamel, and securing intimate contact; that the oxygen liberated by the iron oxide is fixed by the cobalt oxide, preventing excessive bubble formation; that the formation of a dendritic layer associated with good adherence is facilitated by the presence of cobalt; and finally, that iron oxide at the interface is reduced in the presence of cobalt compounds to a lower oxide which is soluble in the enamel.[42] Nickel and manganese oxides are also used in ground coats and sometimes a flash of nickel is plated on the steel base. and these measures are thought to contribute to adherence.[44] It is claimed also that the nickel "dip" lessens the occurrence of "fishscaling," "copperheads" and other defects in the enamel.[45]

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[43] *Private communication* from Mr. Emerson P. Poste, May 26, 1938.

In the dry process of enameling, which is usually employed in the production of cast-iron sanitary-ware, the frit is ground to a fine powder in a dry mill with the addition of opacifiers or coloring agents. The resulting powdered mixture is applied by means of a sieve to the heated surface which has been given a ground coat previously by the wet process, and the part returned to the furnace where the dusted-on coat is fused.

Of particular interest in the chemical industry is the acid-resistant type of sheet-iron enamels. In general, these differ from the enamels used for general purposes in containing higher proportions of silica and feldspar, and lower proportions of fluorides and borax. Titanium oxide is a useful ingredient in enamels of this type.

The firing or "burning" of enamels consists in subjecting the dried coating to a temperature of approximately 790 to 870° C. (1450 to 1600° F.) for a period of 1 to 5 minutes for light ware. For large pieces the heating may be much longer. Cast-iron enameled by the wet process is heated at a somewhat lower temperature, *e.g.*, 625 to 760° C. (1150 to 1400° F.) for 10 to 15 minutes. Each coat is fired separately and in the wet process the surface is allowed to cool to room temperature between coats. In enameling signs the article may be fired from four to eight times depending upon the number of colors.

The furnaces used in firing enameled coatings are generally of the oil or gas-fired muffle type. In recent years, there has been a trend toward the use of continuous furnaces of both the circular and tunnel type, particularly for the firing of small parts. Electrically heated furnaces are being used to an increasing extent.

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[44] *Private communication* from Mr. Emerson P. Poste of Chattanooga, Tenn., April 20, 1938.

[45] Anon., *Steel*, 98, 54 (May, 1936).

The life of enamel coatings depends upon the proper selection of composition to meet a given environment, freedom from coating defects and the avoidance, in use of the equipment, of severe mechanical injury, such as impact of a sharp object or bending over a small radius. Parts are usually designed to prevent their being subjected to mechanical strains. The use of high proportions of silica in enamels for acid resistance has been mentioned. For sign enamels, which must be resistant to weather, somewhat softer compositions are used, but these must be held low in fluorine compounds and low in clay to avoid chalking. In thin sheet-steel stock likely to be subject to slight bending, enamels are applied in coatings as thin as is consistent with complete continuity and reasonably uniform color and opacity.

Various types of ceramic coatings other than vitreous enamels are employed for the protection of metals. In the oil industry, cracking vessels have been protected successfully by coating with a mixture of furnace cement and sand, to which small amounts of short fiber asbestos and waterglass are added, the coating being cured on the surface by heating to 900° F. (482° C.).[46]

Cast-iron and steel pipes are regularly coated on the inside to resist corrosion by pure, and therefore, corrosive waters, salt solutions and sulfur-bearing oils. Concrete coatings are used for the protection of the outside surfaces of pipes against corrosion by salty marsh soils. A dense, rather water-tight mixture consisting of 2 parts of sand to 1 part of cement in a coating thickness of 2 to 4 inches is generally used for this purpose.[47] The alkalinity of the cement maintains the iron surface in a non-corroding condtiion.

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[46] Morrell, J. C., and Faragher, W. F., *Chem. Met. Eng.*, 36, 596 (1929).

[47] Speller, F. N., "Corrosion, Causes and Prevention," 2nd ed., pp. 318, 524, New York, McGraw-Hill Book Company, 1935.

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